

CHARACTERIZATION OF COMPOSITE MEMBRANES WITH THE USE OF ELECTRO CHEMICAL METHODS



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IN
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Under the supervision of :

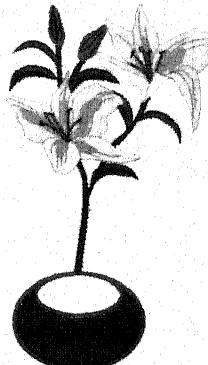
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Submitted by :
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Dedicated to

My Father
Ram Swaroop Rai
Mother
Mrs. Phoolwati Rai
whose support and
unfailing confidence on
me. Never let me lose
Sight of my destination.

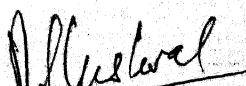


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CERTIFICATE

This is to certify that the thesis entitled "CHARACTERIZATION OF COMPOSITE MEMBRANES WITH THE USE OF ELECTROCHEMICAL METHODS" embodies the original research work of Mr. BHUPENDRA RAI who has worked under the able guidance and supervision of the undersigned in the post graduate department of Chemistry Bipin Bihari (P.G.) College, Jhansi. The candidate has put more than 200 days in the department as required by the university ordinance. The thesis is suitable for the submission to award the degree of "DOCTOR OF PHILOSOPHY" in chemistry from the Bundelkhand University, Jhansi. Such work has not been submitted to any other university.

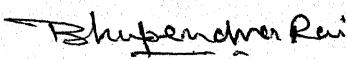
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DECLARATION

I hereby declare that the thesis entitled "CHARACTERIZATION OF COMPOSITE MEMBRANE WITH THE USE OF ELECTROCHEMICAL METHODS" being submitted for the degree of "DOCTOR OF PHILOSOPHY" to the Bundelkhand University, Jhansi (U.P.) is an innovative piece of work carried out with utmost dedication by me and to the best of my knowledge and belief that it has not been submitted elsewhere.



(Bhupendra Rai)

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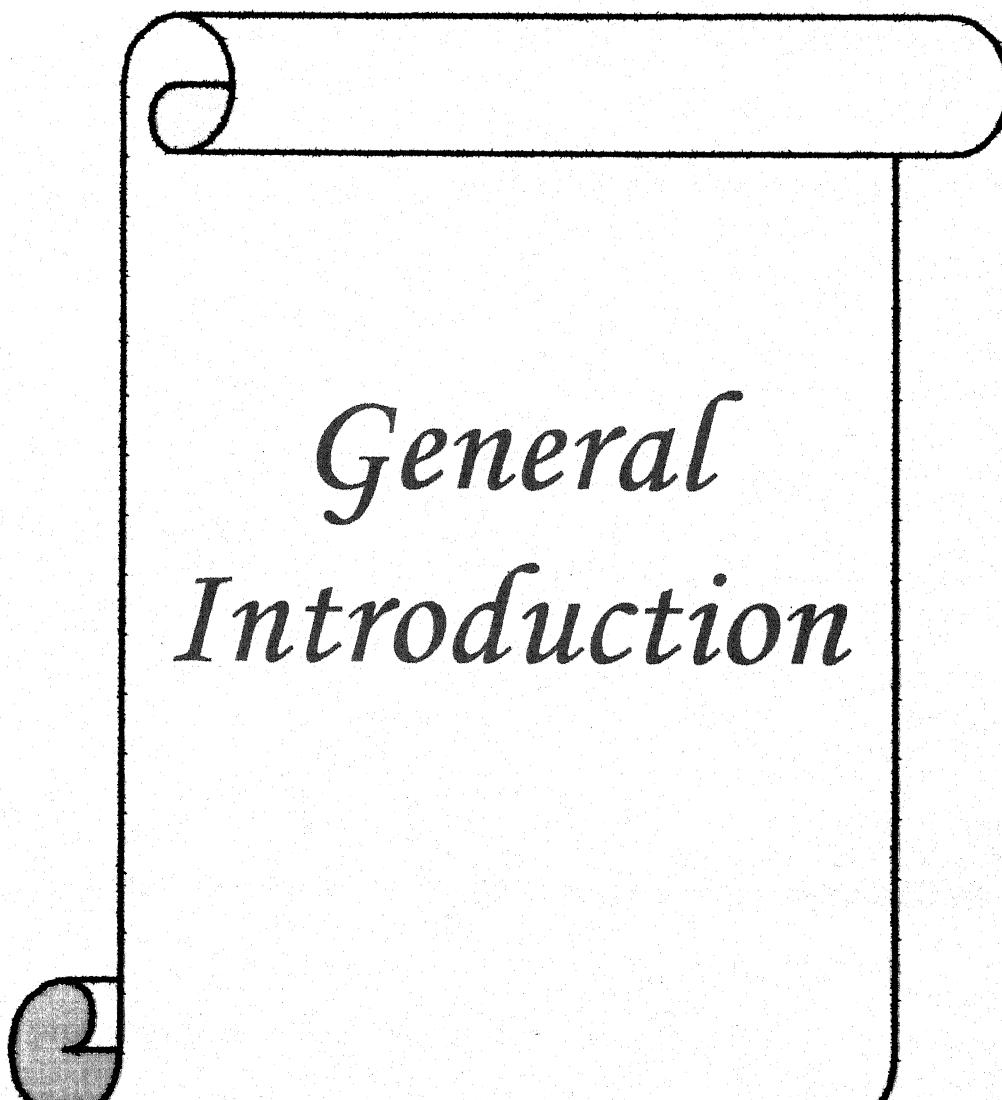
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*General
Introduction*

GENERAL INTRODUCTION

Transport processes occurring across artificial membranes separating different solutions have attracted the attention of chemists, chemical engineers and biologists etc. Chemists and chemical engineers would like to understand the mechanisms of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists, however, would like to use them as simple models for the physiological membranes in order to understand the behavior of complex cell membranes in terms of established physicochemical principles. The recent progress pertaining to membrane diffusion and transport problems have been achieved in varying fields like Chemistry, Bio-chemistry, Physiology, Pharmacology, Biophysics, and Industrial Chemistry etc. in which the starting points and aims have been different. Surface chemistry, Solution theory, Colloid chemistry, Electrochemistry and Thermodynamics etc. have been employed to understand the mechanism of transport in living cells, desalination and electrodics. There are several areas of membrane research which have potentially far-reaching consequences to medicine and chemical industry. Work in this field is contributing significantly to the economic prosperity and physical well being of all mankind.

Moreover Membrane technology has come of age over the past 30 years or so, we have seen the growth of several new industries based on membrane technology. It is a highly fragmented technology, covering such wide-ranging application as reverse osmosis, gas separations, controlled

release pharmaceutical formulations, and the artificial kidney. The scientific and engineering disciplines involved are also varied, and include physical and polymer chemistry, electrochemistry and chemical engineering. But the glue that binds all of these varied applications and disciplines together is transport across membranes.

The literature in book form describing membrane technology and applications is far too extensive to mention. The principal volumes containing significant sections on, or totally devoted to membrane electrochemistry are by Clarke and Nachmansohn (1), Helfferich (2), Spiegler (3,4), Merten (5), Marinsky (6), Stein (7), Cole (8), Lakshminarayanaiah (9-11), Hope (12), Arndt and Roper (13), Polensey (14), Kotyk and Janacek (15) and others. Continuing series are edited by Bittar (16), Eisenman (17), Danielli, Rosenberg and Cadenhead (18). Applications of membrane electrochemistry to yield activity sensing electrodes are amply described in books edited by Eisenman (19) and Durst (20). However, this field has produced such a variety of new measuring devices and has opened so many analytical possibilities in terms of new analysis and new detection systems that it is very likely that additional volumes will soon appear. Numerous recent volumes are concerned, in part, with membrane electrochemistry (21-29).

A precise and complete definition of the word "Membrane" is difficult to make (30), and any complete definition given to cover all the facets of membrane behavior will be incomplete. According to Sollner (30,31) "A membrane is a phase or structure interposed between two phases or

compartments which obstructs or completely prevents gross mass movement between the latter, but permits passage, with various degrees of restriction, of one or several species of particles from the one to the other or between the two adjacent phases or compartments, and which thereby acting as a physicochemical machine transforms with various degrees of efficiency according to its nature and composition of the two adjacent phases or compartments. In simple terms it is described as a phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquids and/or vapors contacting the two surfaces (9). The term heterogeneous has been used to indicate the internal physical structure and external physicochemical performance (30, 32-34). From this point of view, most membranes in general, are to be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous (36).

The notion of homogeneous vs. heterogeneous membranes proves to be an important distinction from the point of view of mass transport. In the dilute solution limit, the friction coefficients for mass transport by diffusion or migration are interconvertible by Onsagar reciprocal relations, and both can be related to jump distances and frequencies according to random walk models. As long as there are no preferred regions of low friction in the membrane, it is isotropic on a molecular level and is considered to be homogeneous. Uniformity of mesh on a molecular scale is another view of homogeneity. Channel free solid and liquid membranes are usually homogeneous, and two phase membranes such as solid crystallites imbedded

in a nonionic resin are clearly heterogeneous. The distinction, however, is not always essential (36).

Membranes may be solid, liquid or gas (37) and the outer phases are usually liquid or solid. Membranes are usually thin in one dimension relative to the other two dimensions. This property is only functional or operational. In order to achieve a measurable chemical change or electrochemical effect and to make chemical or electrochemical measurements on a membrane system in a reasonable time, some transport related property must be susceptible to temporal change. Thus, a change in potential, flux, or concentration (among many varying and measurable quantities) requires membrane thicknesses d such that $d^2/2D$ is comparable with the observation time (D is a mean diffusion coefficient). Although irregularly shaped membranes are conceivable, most theories and experiments are restricted to systems with one dimensional or spherical symmetry such that transport occurs in one dimension, the x direction in parallel-face, planar membranes or along a radius in membrane with spherical shape.

Membranes are considered to be porous or nonporous depending upon the extent of solvent penetration (38). At the nonporous extreme are membranes which are nonionic and contain negligible transportable species at equilibrium. Ceramics, quartz, anthracene crystals, and teflon films between metal electrodes or electrolyte bathing solutions are solid membrane examples. Organic liquid films such as hydrocarbons and fluorocarbons in contact with aqueous electrolytes are liquid membrane examples. At the other extreme are porous membranes, which can be solvated and will contain

components from the outer phases. Among these are nonionic films such as cellophane, inorganic gels, and loosely compressed powders in contact with aqueous solutions. These materials absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. More widely studied are the membranes of polyelectrolytes, aqueous immiscible organic liquid electrolytes (2,9,11,39), various parchment supported inorganic precipitates (40-54), solid ion conducting electrolytes including silver halides, rare earth fluorides, and alkali silicate and alumino-silicate glasses (19,20,55,56). All these materials contain ionic or ionizable groups within the membranes which are capable of transport under diffusive or electric field forces. In addition, these materials possess the property of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion exchangers are surprisingly slow to take up water, while the inorganic salts have no tendency to hydrate. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water (57-59).

Depending on the dielectric constant and solvent penetration, sites are potentially, partially, or even completely ionized. A characteristic of electrolyte membranes is the presence of charged sites (2, 60-62). If ionic groups are fixed in a membrane as $-SO_3^-$ and $-COO^-$ attached to cation exchange resins, the membrane is considered to possess fixed sites, even if protons or metal ions are covalently bonded to the sites. In glasses, the fixed sites are $-SiO^-$ and $-AlO^-$ groups, while in anion exchange resin membranes these are $-N^+$. On the other hand liquid ion exchangers which are water

immiscible such as diesters of phosphoric acid, can be viewed as mobile site membranes. The acid is trapped in the organic phase, while the protons and/or other cations can move in and out of the membrane, the phosphate cannot. Membrane without ionizable groups contain no charge sites. It is important to know that cellulose triacetate, which is initially site free, soon develops negative sites by hydrolysis and oxidation on exposure to aqueous solutions.

The frequent use of "charged" and "uncharged" in the membrane literature is usually unsound electrostatically, but does provide an intuitive chemical description. For example, "charged" membrane usually refer to electrolyte membranes such as solid and liquid ion exchangers where the fixed and mobile sites are the "charges". Actually, these membranes are quasi-electroneutral in their bulk when the thickness is large compared with the Debye thicknesses at each interface. Quasi-electroneutrality means that in any volume element large compared with the distance between ions, the sum of ionic charges $\sum Z_i \bar{C}_i = 0$. In the literature, "uncharged" membranes are those, like cellophane, with no fixed charges. This frequently used literature definition provides no place for lipid bilayer membranes, which are electrostatically neutral only in the absence of charge carriers and in the absence of bathing solutions whose salts possess preferential solubility of anion over cation or vice versa, but are usually electrostatically charged by an excess of ions of one sign in normal operation. Thick hydrocarbon membranes and membranes of diphenyl ether (or derivatives), phthalate, and sebacate esters are generally neutral in the presence of most bathing

electrolytes, but may be charged electrostatically, depending on thickness, in the presence of neutral carrier species which preferentially solubilize ions of one sign. The use of "charged" and "uncharged" to describe electrolyte or non-electrolyte membrane has been discouraged unless the precise electrostatic connotation is involved (36).

Membranes may be broadly classified into natural and artificial. Natural membranes are classified to possess a fundamental unit membrane structure which is a bimolecular leaflet of lipid with their polar groups oriented towards the two aqueous phases of the cell, and protein is supposed to exist close to the polar heads of the leaflet. This type of the universal structure is absent in artificial membranes. Eisenman et. al. (63) have given a classification of these membranes based on their structures.

Unlike the classification based on membrane structure, membranes are usually classified either on the basis of their nature, i.e., coherent gel or otherwise, or on the nature of the chemical reaction involved in their formation, i.e., addition or condensation reaction. The efforts of various workers have been directed towards : (A) preparing membranes with good chemical and mechanical stability and favourable electrical performance suitable for fundamental transport studies and for applications in some industrial operations such as the treatment of brakish water, saline water conversion etc., (B) building suitable models to mimic the properties of natural membranes, and (C) preparing composite membranes containing cationic and anionic groups in suitable arrangement to demonstrate and to study the physicochemical phenomena associated with the rectification of

alternating current and other special membranes for specific purposes. It is worthwhile to mention that most of the work concerning category (A) seems to be directed towards finding suitable membrane materials for fabricating a structure for effective desalting sea water by application of pressure. The most commonly used material for casting a membrane for desalination is cellulose acetate although, polymethacrylic acid (PMA), phenolsulfonic acid (PSA), polystyrene sulfonic acid (PSSA) and cellulose esters have proved very useful (64). A number of investigators in recent years have prepared membranes from cellulose acetate under varying conditions and used them to understand the mechanism of water flow (3,4,5,65-79). In category (B) bilayer membranes, first generated by Mueller (80), have most widely been used as model for living cells and the studies have given somewhat a better understanding of the structure and function of the natural membranes. Recently a number of bilayer membranes and their studies have been reported (81, 83) The membranes of category (C) are quite numerous (10,36,84,85).

Theories on the transport of charged or uncharged particles across membranes can be roughly divided according to Schlogl (86) into the following groups.

Group one considers the membrane as a surface of discontinuity setting up different resistances to the passage of the various molecular or ionic species (87, 88). The driving forces are the differences of the general chemical potential between the two outer media (Differences of pressure or electrical chemical potential are included in the general chemical potential).

Group two considers the membrane as a quasihomogeneous intermediate phase of finite thickness in which the local gradients of the general chemical potential act as driving forces (60,61,89-95). Convection may also contribute to particle transport within the membrane.

Group three considers the membrane as a series of potential energy barriers lying one behind the other, thus forming, in contrast to group two, an inhomogeneous intermediate phase (96-98). An (irregular) spatial lattice is formed due to the higher probability of finding a particle in the positions between the activation thresholds. The driving forces arise from the differences between the transition probabilities in opposite directions perpendicular to the membrane.

This grouping attempts to classify the various mathematical approaches, according to the ideal models on which they are based. It is in fact too schematic, as many theories occupy intermediate positions. No author is likely to take the view that one of these treatments is right and the others wrong. The various descriptions supplement each other, and depending on the system under consideration, one of the three will prove the most suitable. It may be shown, for example, that when the number of activation thresholds becomes very large, and the distance between the lattice points sufficiently small, then groups 3 and 2 merge into each other. A transition is also found between group 1 and 2 (86).

Unlike group 3, group 1 and 2 can be classified in the general scheme of irreversible thermodynamics. In group 1 as well as in group 2, linear relationships are assumed between the particle fluxes and the driving forces.

Owing to the differing characters of the driving forces, group 1 is treated according to the method of "discontinuous systems", and group 2 according to that of "continuous systems". An integration in group 2 across the membrane does not as a rule yield a linear relationship between the flux and the general chemical potential differences. Only for sufficiently small differences does group 2 merge into group 1 after integration. In this sense group 2 is more general than group 1. Group 2 is, however, inferior to group 1 in that a number of idealizations must be assumed before an explicit integration can be affected. Kirkwood (99) finds a correction between group 1 and 2. His initial flux equation differs from that normally used in the treatment of "continuous systems" in irreversible thermodynamics. This treatment of Kirkwood has been developed and modified by Schlogl. On a broad basis, it may be said that the theories of group 1 are based on the ideas of classical thermodynamic or quasi-thermodynamics which is restricted to isothermal systems. The theories of group 2, apart from being more rigorous and realistic allow a better description and understanding of transport phenomena in membranes and are useful in dealing with non-isothermal systems. The theories of group 3 provide a general and unified view applicable to systems of differing degrees of complexity. Many of the theories based on the Nernst-Plank flux equation are placed in the first group whereas those dealing with the principles of irreversible thermodynamics and the theory of absolute reaction rates are placed in the 2nd and 3rd groups respectively.

The theories of the first group have the advantage of being relatively simple. For ion-exchange membranes, However, they are often inadequate. These theories deal chiefly with processes occurring within the membrane. For such a purpose the theories of the second group are proper choice.

The most important theories of the second group are based either on quasi-thermodynamics or on thermodynamic of irreversible processes. the fundamental difference between these two approaches are summarized below.

Quasi-thermodynamics is not interested in particle fluxes. One might say that the quasi-thermodynamic approach consists in taking a snapshot of the system and calculating the emf from the charges which a reversible electric current would produce in the system if it were "frozen" in the state in which the photographic picture was taken. This procedure gives directly the emf of the cell. No model is needed. Taking the snapshot, however, is often not as simple as it may seem. A rigorous treatment would require the knowledge of the composition of every differential layer of the diffusion zone (i.e., the concentration profiles of all species.) Since obtaining this information experimentally is usually too lengthy a task or even quite impossible, the quasi-thermodynamic treatment is forced to make assumption about the condition of the system.

The thermodynamics of irreversible processes (100). in contrast to quasi-thermodynamics, does not require prior knowledge of the concentration profiles. The set of equations of thermodynamics of irreversible processes interrelates all occuring "fluxes" (of species electric

current, heat etc.) and "driving forces" (gradients of chemical potential, electric potential, temperature etc.). From measurements of a sufficient number of "phenomenological coefficients", all fluxes and forces and hence also the emf can be calculated, without knowledge of the profiles and without using the concept of "reversible energy production" on which quasi-thermodynamics is based. Furthermore, thermodynamics of irreversible processes is applicable also to nonisothermal systems and includes coupling of fluxes which is not covered by quasi-thermodynamics. It may be mentioned here that the discipline of irreversible thermodynamics provides a precise mathematical description of the processes of transport and diffusion in membranes systems. Its application to membrane processes is a natural development of the basic theory of Onsagar (101) and has been developed by Staverman (88), Kedem (102), Katchalsky (100), Caplan (103), Mears (104), Spiegler (3,4), Rastogi (105), Narebska (106), Beg (107) and others in an extensive and expanding literature.

The theory of absolute reaction rate has been applied to diffusion processes in membranes by several investigators. Zwolinski, Eyring and Reese (98), considered the diffusion process as one of the basic phenomena for sustaining the growth and development of plants and organism. They presented a detailed kinetic approach to diffusion which clarifies much established concepts and provide impetus to a fresh approach to the problems in the field of biological diffusion. The absolute reaction rates theory treatment of diffusion and membrane permeability provides a general unified point of view applicable to systems of varying degrees of

complexity. It is equally adoptable to the treatment of the permeabilities of membranes to electrolytes, to non-electrolytes under the driving forces of a concentration gradient, activity gradient, and external and internal potential gradients. Zwolinski, Eyring and Reese (98) treatise on membrane diffusion is based on the "activated state" or the "transition state" theory.

Laidler and Shuler (97) have also treated the kinetics of membranes transport under steady state conditions. They employ similar principles and express the rate constant of the over all process of surface penetration in terms of a number of specific rate constants. Various special cases are considered and discussed with reference to the experimental data. They developed flux equations for solvent and solute especially as a function of the osmotic and hydrostatic pressures across the membrane. Tien and Ting (108) and recently, others (83, 109), have applied the theory of absolute reaction rates to diffusion processes through Bilayer lipid Membranes (BLM) and have derived various thermodynamic quantities like free energy of activation, enthalpy of activation and entropy of activation etc.

Application of electrochemistry in membrane studies is pertinent at three levels (36). One is the development of techniques with application to experimental phenomenology including current-voltage-time concentration behavior. A second is the mathematical modeling implied by experiment and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties and includes determination of theoretical parameters by electrical methods and by complementary non-electrochemical methods: physical, optical, esr, nmr,

Raman, fluorescence, T-jump techniques, etc. From transient and steady state measurement of current or membrane potential as a function of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to modeling begins with the assumption of the membrane as a linear system to which laws of network theory may be applied. Another begins by solution of basic electro-diffusion laws of transport with equilibrium or kinetic boundary conditions in order to deduce forms for system functions which satisfy the data.

The most important contribution of electrochemists to membrane electrochemistry is the transfer of perspective and wisdom to the new area. There are many *sine qua nons* in electrochemistry which have occurred through extensive studies of electrolytes and electrolyte /membrane interfaces. Electrochemists have learned to subdivide systems into interfacial bulk processes and to expect effects of dielectric constant (complex formation, ion pairing), effects of short-range forces (adsorption of charged and uncharged species with, possibly, changes in rates of interfacial processes), effects of high fields near surfaces (Wien Effect, and dielectric saturation, for example), and the important effect of local potentials on rates of interfacial processes (irreversible charge transfers, psi effects, etc.). Inasmuch as the presence of the space charge at interfaces is a natural consequence of the continuity of potential from one phase to another, the presence of space charge and space charge mediated effects in membrane systems is anticipated.

In this thesis studies of transport properties of parchment supported inorganic precipitate membranes when they are used to separate various

aqueous electrolyte solutions are reported. The membrane electrolyte system has been considered to contain four chemical species, counterion 1, coion 2, water 3 and fourth the membrane matrix which carries fixed inorganic groups and excludes the possibility of chemical reaction within the membrane. The membrane matrix has, therefore, been considered to consist of fixed charge and adjacent polymer segments which together constitute the repeat unit of the matrix. It is, therefore, possible that kinetic coupling interaction of membrane matrix will include not only the contribution of fixed charge, but also specific polymer effects if such exist. This is an important qualification to the description of the species four as simply as ion, although it appears from earlier studies that such effects are small (105-107).

The discussion has mainly been restricted to commenting on only a few points concerning the following ionic processes in the membrane systems, "permeability phenomena."

- 1- Ionic transport "flux"
- 2- Membrane potential
- 3- Electrical conductivity
- 4- Ionic distribution equilibria
- 5- Spatial distribution of the ions and the potential within the membrane .

The thesis has been presented under the following heads :-

1- MEMBRANE CHARGE DENSITY :

This portion deals with the measurements of membrane potential across parchment supported cobalt and nickel phosphate membranes using various 1:1 electrolytes at different concentrations and under isothermal

condition for the evaluation of thermodynamically effective fixed charge density of the membranes as well as to examine the validity of the recently developed theories for membrane potential including those based on the thermodynamics of irreversible processes.

2- DIFFUSION OF ELECTROLYTES :

This portion deals with the evaluation of diffusion rates of a number of 1:1, 2:1 and 3:1 electrolytes through parchment supported cobalt and nickel phosphate membranes at different temperatures. Diffusion coefficient and various thermodynamic parameters have been calculated in order to understand the mechanism of ion permeation through the membranes.

3- BI-IONIC POTENTIAL AND TEST OF THEORIES :

This portion restrict the discussion upto the characterization of the membranes with the help of membrane potential and membrane bi-ionic potential. Theoretical values of membrane bi-ionic potential evaluated using the recently developed theories and their comparision with experimental values not only the test of theories but also one of the best method of characterization of the membranes.

REFERENCES

1. H.T. Clarks and D. Nachmansohn, eds., in "Ion Transport across Membranes", Academic Press, New York, (1954).
2. F. Helfferich, Ion Exchange, McGraw-Hill, New York, (1962).
3. K.S. Spiegler, "Salt Water Purification", Wiley, New York, (1962).
4. K.S. Spiegler, ed., "Principles of Desalination", Academic Press, New York, (1966).
5. U. Merten, ed., "Desalination by Reverse Osmosis", M.I.T. Press, Cambridge, Massa Chusetts, (1966).
6. J.A. Marinsky, ed., in "Ion Exchange", Dekker, New York, (1966).
7. W.D. Stein, "The Movement of Molecules across Cell Membranes", Academic Press, New York, (1967).
8. K.S. Cole, Membranes, Ions and Impulses, University of California Press, Berkeley, (1968).
9. N. Lakshminarayanaiah, "Transport Phenomena in Membranes", Academic Press, New York, (1969).
10. N. Lakshminarayanaiah, "Membrane Electrodes", Academic Press, New York, (1976).
11. N. Lakshminarayanaiah, Electrochemistry Specialist Periodical Reports, Vol. 4, Chemical Society London, 167, (1974).
12. A.B. Hope, "Ion Transport and Membrane", University Park Press, Baltimore, Md., (1971).
13. R.A. Arndt and L.D. Roper, "Simple Membrane Electro- diffusion Theory", University Publications, PBSM, Blacksburg, Va., (1972).

14. R. Polensey, "Bioelectric Phenomena", McGraw-Hill, New York, (1969).
15. A. Kotyk and K. Janacek, "Cell Membrane Transport, Principles and Techniques", Plenum Press, New York, (1970).
16. E.E. Bittar, Ed., "Membrane and Ion Transport", Vol. 1, Interscience, New York, (1970).
17. G. Eisenman, "Membranes", Dekker, New York, Vol. 1, (1972); Vol. 2 (1973).
18. J.F. Danielli, M.D. Rosenberg and D.A. Cadenhead, Eds., "Progress in Surface and Membrane Science", Vol. 6, Academic Press, New York, (1973).
19. G. Eisenman, Ed., "Glass Electrodes for Hydrogen and Other Cations", Dekker, New York, (1967).
20. R.A. Durst, Ed., "Ion Selective Electrodes", National Bureau of Standards, Special Pub. # 314, U.S. Government Printing Office, Washington, D.C., (1969).
21. E.J. Harris, Ed., "Transport and Accumulation in Biological Systems", 3rd ed., University Park Press, Baltimore, Md., (1972).
22. D.C. Tosteson, Ed., "Symposium of Molecular Basis of Membrane Function", Prentice- Hall, Englewood Cliffs, N.J., (1969).
23. M. Kotani, Ed., "Advance in Biophysics", Vol. 2, University of Tokyo Press, University Park Press, Baltimore, Md., (1971).
24. F. Snell, J. Walker, G. Iverson and J. Lam, Eds., "Physical Principles of Biological Membranes", Gordon and Breach, New York, (1970).

25. J.A. Marinsky and Y. Marcus, Eds., "Ion Exchange and Solvent Extraction", Vol. 1-6, Dekker, New York, (1969-1974).
26. K. Sollner, in Diffusion Processes, G.N. Sherwood, A.V. Chadwick, W.M. Muir and F.L. Swinton, Eds., Gordon and Breach, New York, 655, (1971).
27. S. Saurirajan and T. Matsudera, "Reverse Osmosis-Ultra filtration process principles", NRCC, Canada (1985).
28. R.E. Kesting "Synthetic Polymeric Membrane - A Structural prospective", Wiley, New York, (1995).
29. S.P. Nues, K.V. Peinemann, Membranes Technology in the Chemical Industry, Wiley - VCH, Verlag GmbH, (2001).
30. K. Sollner, In "Electrochemistry in Biology and Medicine", (T. Shedlovsky, ed.), P. 50, Wiley, New York, (1955).
31. K. Sollner, J. Phys. Chem., 49, 47 (1945).
32. J.A. Kitchener, in "Modern Aspect of Electrochemistry", (J.O'M Bockris, ed.), Vol. 2, P. 154, Butterworths, London, (1959).
33. V. Subrahmanyam and N. Lakshminarayanaiah, Current Sci. (India), 29, 307 (1960).
34. R.N. Rickles and H.Z. Friedlander, Chem. Eng., 73, 163 (1966)
35. F. Helfferich, ref. 2, p. 61.
36. R.P. Buck, CRC Critical Reviews in Analytical Chemistry, P. 323, (1976).
37. J.E.B. Randles, Trans. Faraday Soc., 52, 1573 (1956).
38. N. Lakshminarayanaiah, ref. 9, Chap. 2.

39. N. Lakshminarayanaiah, Electrochemistry Specialist Periodical Reports, Vol. 2, Chemical Society London, p. 203 (1972).
40. M.N. Beg, F.A. Siddiqi and R.S. Kushwaha Can. J. Chem, 55, 1680 (1977).
41. M.N. Beg, F.A. Siddiqi, R.S. Kushwaha and M. Arshad, J. Membrane, Sci. 2, 365 (1977)
42. M.N. Beg, F.A. Siddiqi, R.S. Kushwaha and I. Altaf, J. Electroanal. Chem., 89, 141, (1978).
43. F.A. Siddiqi, M.N. Beg and P. Prakash, Ind. J. Chem. 16A, 7 (1978).
44. F.A. Siddiqi, M.N. Beg, M.I.R. Khan, A. Haq, S.K. Saxena and B. Islam, Can. J. Chem., 56, 2205 (1978).
45. R.S. Kushwaha, M.A. Ansari, N. Akhtar and P. Singh, Ind. J. of Chem., Vol. 31 A, 439 (1992).
46. M.A. Ansari, R.S. Kushwaha, A.K. Verma and C.M. Gupta, U. Scientist, Phyl. Sciences, Vol. 8, 1, 19, (1996).
47. R.S. Kushwaha, R. Tiwari, A. Gupta and M.A. Ansari, Flora and Fauna, 3, 1, (1997).
48. R.S. Kushwaha, H.P.S. Sengar, A. Gupta, R. Tiwari, and M.A. Ansari, Flora and Fauna, 4, 2, 93 (1998).
49. R.S. Kushwaha, B. Rai, M. Kumar and M.A. Ansari, Proc., BRMUW, 2004 (In press).
50. R.S. Kushwaha and M.A. Ansari J. Ind. Council of chemists, Vol., 23, No. 1, 32 (2006)

51. R.S. Kushwaha, A. Kumar, R.B. Sharma and S. Agarwal, *Flora and Fauna*, 7, 9 (2001).
52. R.S. Kushwaha, M.A. Ansari and R. Tiwari, *Ind. J. of Chem.*, Vol. 40A, 270 (2001).
53. R.S. Kushwaha, M.A. Ansari, A. Bhartiya, *Chem. Environ. Res.*, 12, (3&4) 26, (2003).
54. R.S. Kushwaha, S. Agarwal and M.A. Ansari, *J. Ind. Council Chemists*. Vol. 21, No. 2, 10, (2004).
55. R.P. Buck and E.C. Toren, *Anal. Chem.*, 42, 284R (1970).
56. R.P. Buck, *Anal. Chem.*, 44, 270R (1972); 44, 28R (1974).
57. J.R. Sandifer and R.P. Buck, *J. Electroanal. Chem., Interfacial Electrochem*, 56, 385 (1974).
58. A. Wikby and B. Karlberg, *Electrochim. Acta.*, 19, 323 (1974).
59. A. Wikby, *Electrochim. Acta.*, 19, 329 (1974).
60. T. Teorell, *Proc. Soc. Exp. Biol.* 33, 282 (1935); *Proc. Natl. Acad. Sci. (U.S.A.)*, 21, 152 (1935); *Z. Electrochem.*, 55, 460 (1951); *Prog. Biophys. Chem.*, 3, 385 (1953).
61. K.H. Meyer and J.F. Sievers, *Helv. Chim. Acta.*, 19, 649 (1936); 19, 665 (1936); 19, 987 (1936).
62. T. Teorell, *Discuss. Faraday Soc.*, No. 21, 9 (1956).
63. G. Eisenman, J.P. Sandblom, and J.L. Walker, Jr., *Science*, 155, 965 (1967).
64. N. Lakshminarayanaiah, ref. 9, p. 12.

65. S. Kimura and S. Sorirajan, A.I. Ch. E.J., 13, 497 (1967); Ind. Eng. Chem. Process Design Develop., 7, 41 (1968).
66. T.S. Govindan S. Sorirajan, Ind. Eng. Process Design Develop., 5, 422 (1966).
67. H.K. Lonsdale, U. Merten and R.L. Riley, J. Appl. Polymer Sci., 9, 1341 (1965).
68. R.L. Riley, H.K. Lonsdale, C.R. Lyons, and U. Merten, J. Appl. Polymer Sci., 11, 2143 (1967).
69. H.K. Lonsdale, U. Merten and M. Tagami, J. Appl. Polymer Sci., 11, 1807 (1967); J.S. Johnson, "Rivers Osmosis Membrane Research" (H.K. Lonsdale and H.E. Podall, Eds.), Plenum, New York, (1972).
70. H.K. Lonsdale, R.L. Riley, C.E. Milstead, L.D. LaGrange, A.S. Douglas, and S.B. Sachs, U.S. Officer Saline Water, Res. Develop. Progr. Rep., No. 577, p. 143 (1970).
71. E. Drioli, H.K. Lonsdale and W. Pusch, J. Colloid Interface Sci., 51 (3) 355 (1975).
72. H.K. Lonsdale, B.P. Cross, F.M. Graber and C.E. Milstead, J. Macromol Sci., Phys., 5 (1), 167 (1971).
73. H.K. Lonsdale, R.L. Riley, C.R. Lyons and D.P. Carosella, Jr., Membrane Processes Ind. Biomed., Proc. Symp. P. 101-22 (1970).
74. H.K. Lonsdale, W. Pusch and A. Walch, J. Chem. Soc., Faraday Trans. 1, 71 (13), 501 (1975).
75. M.D. Reboiras, J. Membrane Sci, 114, 105 (1996).

76. A.N. Nagappa, P.L. Kole, P.V. Pandi, R.T. patil, K.Zeeyyauddin and I. Shanmukha, Ind. J. of Biochemistry & Biophysics, 41, 48 (2004).
77. K. Singh and A.K. Tiwari, J. Membrane Science, 34, 155 (1987).
78. K. Singh and V.K. Shani, J. Membrane Sci., 59, 27 (1999).
79. D. Ruan L. Zhang, Y. Mao, M. Zeng, X. Li, J. Membrane Sci., 241, 265 (2004).
80. P. Mueller, D.O. Rudin, H.T. Tien and W.C. Wescott, Circulation 26, 1167 (1962); Nature, 194, 979 (1962); J. Phys. Chem., 67, 534 (1963).
81. Y.F. Zhang, X-P Hau, G. Wu, R.C. Li, X.W. Qiao, H.T.Tien, A. Ottova., Electrochemistry Communications, 1, 238 (1999)
82. J.S. Ye, A. Ottova, H.T. Tien, F.S. Sheu, Electrochemistry Communications, 3, 580 (2001).
83. K.E. Alcantara, J.F. Rusling, Electrochemistry. Communications 7, 223, (2005)
84. J. Koryta, Anal. Chim. Acta., 91, 1 (1977); 61, 329 (1972).
85. R.P. Buck, Analytical Chemistry, 50, No. 5, 17 R (1978).
86. R. Schlogl, Discuss. Faraday Soc., No. 21, 46 (1956).
87. P. Masur and J.T.G. Overbeek, Rec. Trav. Chim., 70, 83 (1951).
88. A.J. Staverman, Trans. Faraday Soc., 48, 176 (1952).
89. J.S. Mackie and P. Meares, Proc. Roy. Soc. A., 232, 498 (1955).
90. D.E. Goldman, J. Gen. Physiol., 27, 37 (1943).
91. A.L. Hodgkin and B. Katz, J. Physiol., 108, 37 (1949).
92. G. Schmid, Z. Electrochem, 55, 295 (1951); 56, 181 (1952).
93. P.B. Lorenz, J. Physic. Chem., 56, 775 (1952).

94. R. Schlogl, Z. Physik. Chem. N.F., 1, 305 (1954).
95. G. Scatchard, J. Amer. Chem. Soc., 75, 2883 (1953).
96. H. Davison and J.F. Danielli, The Permeability of Natural Membranes, Chap. 21, Macmillan, New York, (1943).
97. K.J. Laidler and K.E. Shuler, J. Chem. Phys., 17, 851 (1949).
98. B.J. Swolinski, Eyring and Reese, J. Physic. Chem., 53, 1426 (1949).
99. J.G. Kirkwood, Ion Transport across Membranes, (H.T. Clarke, ed.), P. 119, Academic press, New York, (1954).
100. A. Katchalsky and P.F. Curran, "Non equilibrium Thermodynamics", Harvard Univ. Press, Cambridge Massachusetts, (1965).
101. L. Onsager, Ann. N.Y. Acad. Sci., 46, 241 (1945).
102. O. Kedem and A. Essing, J. Gen. Physiol., 48, 1047 (1965).
103. S.R. Caplan and D.C. Mickulecky, in "Ion Exchange", (J.A. Maxinsky, ed.), Dekker, New York, Chap. 1, (1966).
104. P. Mears, J.F. Thain and D.G. Dawson, in "Membranes A Series of Advance", (G. Eisenman, ed.), Dekker, New York, Chap. 2, (1972).
105. R.P. Rastogi, and K.M. Jha, J. Phys. Chem., 70, 1017 (1960); Trans. Faraday Soc., 62, 585 (1966);
(b) R.P. Rastogi, K. Singh and B.M. Misra, Desalination, 3, 32 (1967);
(c) R.P. Rastogi, S.N. Singh, and M.L. Srivastava, J. Phys. Chem., 74, 1969 (1970); (d) R.P. Rastogi, K. Singh and J. Singh, J. Phys. Chem., 79, 2574 (1975); (e) R.P. Rastogi and Ram Shabd, J. Phys. Chem., 81, 1953 (1977).
106. A. Narebska and S. Kotter, J. Membrane Sci., 30, 141 (1987).

107. M.N. Beg, M.A. Matin, *J. membrane Sci.*, 196, 95 (2002).
108. H. T. Tien and H.P. Ting, *J. Colloid and Interface Sci.*, 27, 702 (1968).
109. M. Karabaliiev, V. Kochev, *Electrochemistry communications* 3, 742, (2001).
110. H. Ferguson, C.R. Gardner and R. Paterson, *J.C.S. Faraday I.*, 68, 2021 (1972).
111. R. Paterson and C.R. Gardner, *J. Chem., Soc., A.*, 2254 (1971).
112. E. Samson, and J. Marchand, *J. colloid and Interface Sci.*, 215, 1 (1999).

Chapter :I

*Evaluation
of Effective
Fixed Charge
Density*

INTRODUCTION

One of the most consistent properties of biological system is the presence of a voltage across the cellular surfaces. The mechanism where by this potential arises is still in dispute. Some consider it to be diffusion potential while others suggest the voltage to be an adsorption potential (1). Teorell (2,3) considered the presence of charge on the membrane skeleton responsible for the development of potential across it. Based of fixed charge concept a number of theoretical equations for membrane potential, developed across a charged membrane separating two electrolytic solutions, have been derived and tested using, generally, model membranes.

Chakravarti et. al. (4) Characterise the membranes by determining the effective fixed charge density of cation exchange membranes by three different methods based on non-equilibrium thermodynamics. Kehar Singh et. al (5) used the mixture of electrolytes for the measurement of membrane potential and evaluated charge density of the membranes for their characterization. Similarly, many investigators (6-8) have also got their peculiar position regarding the electro chemical characterization of different types of membranes with the help of various theories derived for membrane electrical potential and conductance values based on the irreversible thermodynamics.

In this chapter, the evaluation of effective fixed charge density of parchment supported nickel and cobalt phosphate membranes from potential measurements and using the most recently developed methods of

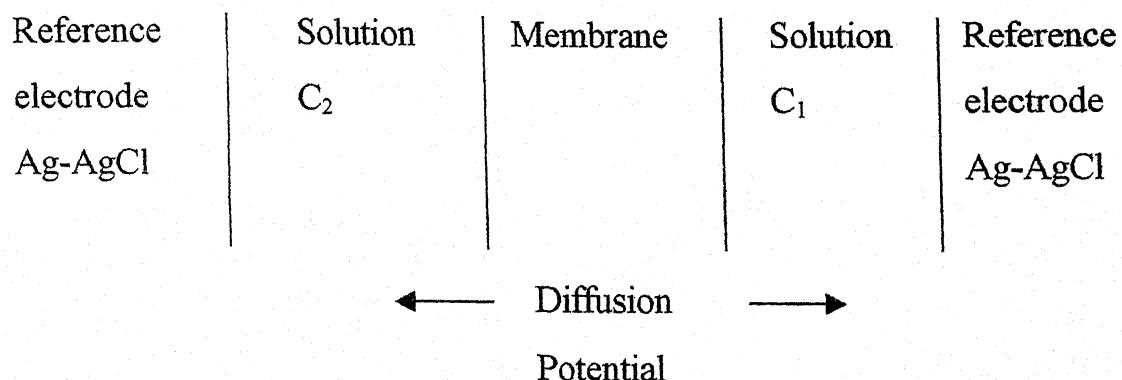
Kobatake et al. (9-20), and Tasaka et al. (21) including the generally used and widely accepted method of Teorell-Meyer and Sievers (2,3) are described. This is in order to substantiate our earlier findings, on the basis of Eisenman-Sherry model of membrane selectivity, that parchment supported membranes possess small density of fixed charge groups on the membrane matrix as well as to test the validity of the recently developed theories for membrane potential.

EXPERIMENTAL

Parchment supported cobalt phosphate and nickel phosphate membranes were prepared by the method of interaction suggested by Kushwaha et. al. (24) and were used here for membrane potential measurements. Solutions used for the preparation of cobalt and nickel phosphate membrane were as follows:

Membrane	Solution I	Solution II
Cobalt phosphate	Co (II) chloride (0.2M)	Trisodium ortho phosphate (0.2M)
Nickel phosphate	Ni (II) chloride (0.2M)	Trisodium ortho phosphate (0.2M)

The membranes were washed with demineralized water to remove free electrolytes completely electro chemical cells of the type.



Were used for measuring membrane potentials. The reference electrodes used were reversible Ag-AgCl standing in chloride solutions. The total potential difference between Ag-AgCl electrodes placed on either side of the membrane is the algebraic sum of the electrode potential, i.e., concentration potential and the membrane potential E_m (22,23). A tenfold difference in concentration of chloride solutions (i.e., $C_2/C_1=10$) was maintained and measurements were made by a pye-precision potentiometer (No. 7568). The solutions were replaced by fresh solutions and when there was no change in potential with the addition of fresh solutions, with constant vigorous stirring by a pairs of magnetic stirrers. It was taken as the true total potential difference across the Ag-AgCl electrodes. In both the membranes it could be reproduced within a few tenths of an mV. The whole cell was immersed in a water thermostat maintained at $25 \pm 0.1^\circ\text{C}$. The various salt solutions (Chlorides of Li^+ , Na^+ and K^+) were prepared from BDH, AR grade chemicals and deionized water.

RESULT AND DISCUSSION

The values of membrane potential E_m measured experimentally across both cobalt phosphate and nickel phosphate membranes are given in Tables 1 and 2, and are also plotted in Figs. 1 and 2 against $\log (C_1+C_2)/2$.

TABLE-1

The Values of The Observed Membrane Potential E_m (mV) Across Cobalt Phosphate Membrane At $25 \pm 0.1^\circ\text{C}$

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (mol/l)			
$1 \times 10^{-1}/1 \times 10^{-2}$	-34.3	-38.7	-35.0
$5 \times 10^{-2}/5 \times 10^{-3}$	-31.4	-36.8	-32.6
$1 \times 10^{-2}/1 \times 10^{-3}$	-28.5	-21.7	-16.4
$5 \times 10^{-3}/5 \times 10^{-4}$	-10.5	-14.5	-10.4
$1 \times 10^{-3}/1 \times 10^{-4}$	1.5	-5.0	5.0
$5 \times 10^{-4}/5 \times 10^{-5}$	9.0	10.0	15.5
$1 \times 10^{-4}/1 \times 10^{-5}$	10.0	15.0	20.0

TABLE-2

The Values of The Observed Membrane Potential E_m (mV) Across Nickel Phosphate Membrane At $25 \pm 0.1^\circ\text{C}$

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (mol/l)			
$1 \times 10^{-1}/1 \times 10^{-2}$	-42.4	-40.0	-40.5
$5 \times 10^{-2}/5 \times 10^{-3}$	-40.3	-40.3	-38.0
$1 \times 10^{-2}/1 \times 10^{-3}$	-32.0	-24.5	-21.5
$5 \times 10^{-3}/5 \times 10^{-4}$	-15.0	-13.0	-6.9
$1 \times 10^{-3}/1 \times 10^{-4}$	1.5	9.0	4.5
$5 \times 10^{-4}/5 \times 10^{-5}$	10.3	10.3	8.0
$1 \times 10^{-4}/1 \times 10^{-5}$	12.5	12.5	15.3

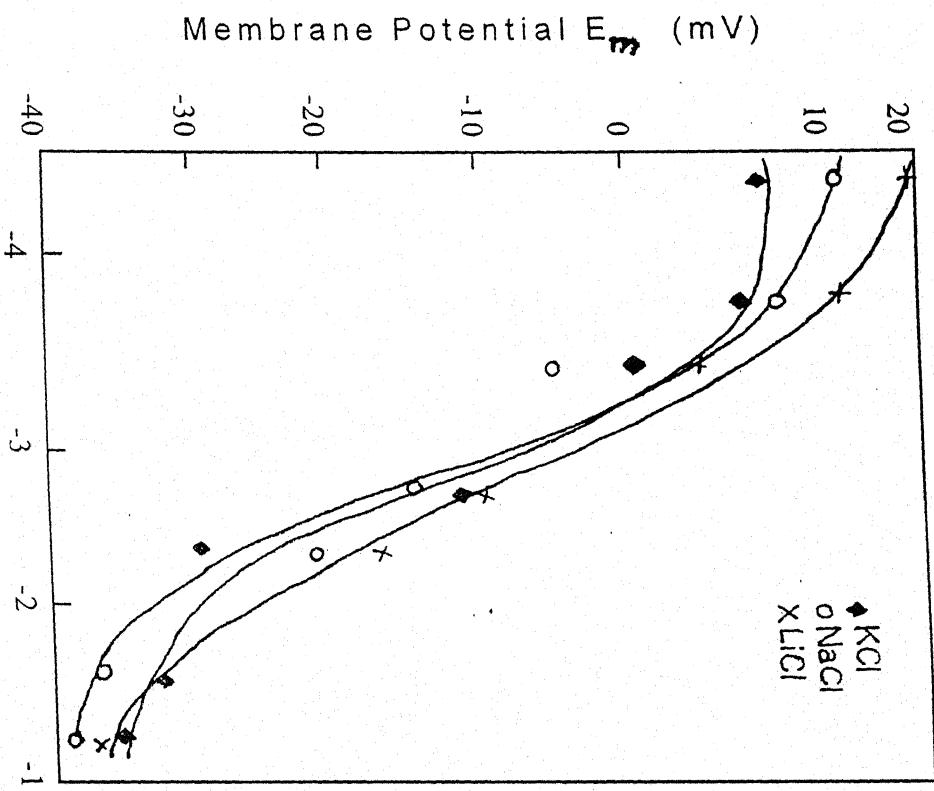


FIG. 1

PLOTS MEMBRANE POTENTIAL E_m (mV) AGAINST $\log (C_1 + C_2)/2$ USING 1:1 ELECTROLYTES ACROSS (A) COBALT PHOSPHATE AND (B) NICKEL PHOSPHATE MEMBRANES

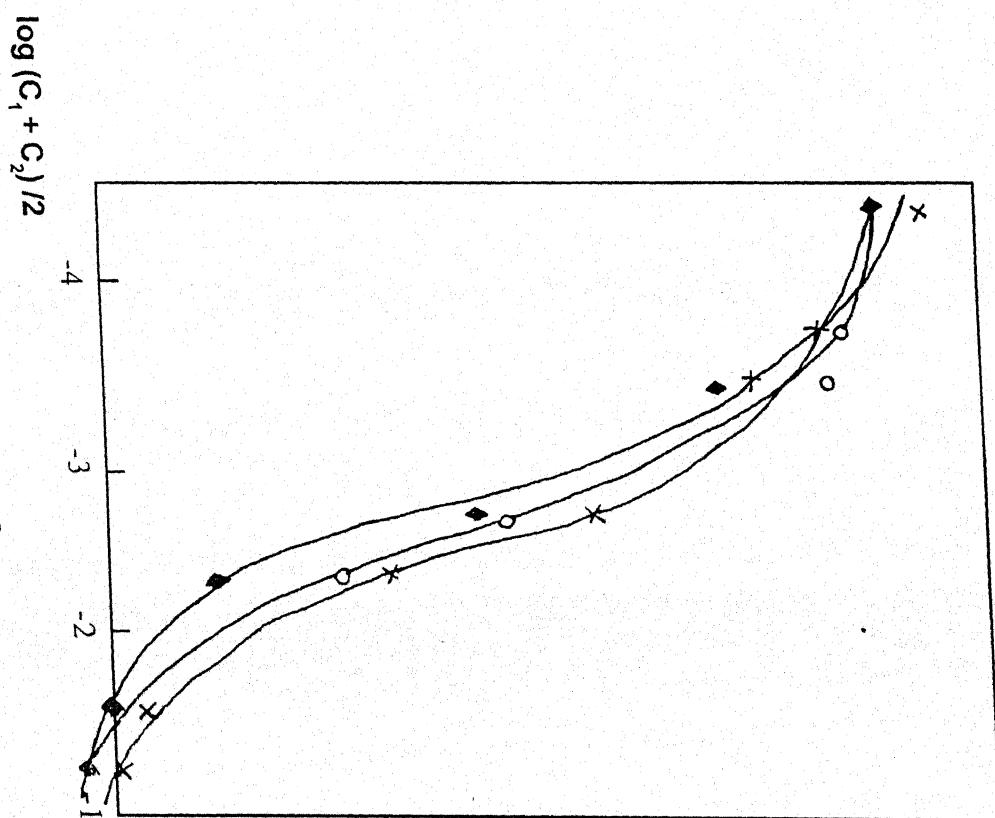


FIG. 2

Parchment supported inorganic precipitate membranes have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations (24-33). This property is attributed to the presence of a net charge on the membrane probably due to adsorption of anions or cations. The quantity of charge required to generate potentials, particularly when dilute solutions are used, is small. This, of course, is dependent on the porosity of the membrane. If the membrane pores are too wide, any amount of charge on the membrane does little to generate good potentials. But if the membrane pores are narrow, a little charge on it can produce ideal potentials according to the Nernst-equation.

$$E_m = \frac{RT}{F} \ln a_1 / a_2 \quad (1)$$

Where a_1 and a_2 are the activities of the two solutions on either side of the membrane, E_m is the membrane potential and R, T and F have their usual significance.

An interesting point with the value of E_m for cobalt and nickel phosphate parchment supported membranes is the fact that these are positive when the membrane is separating dilute solutions of the electrolytes (i.e., dilute side C_1 taken as +ve). This means that the membrane is cation selective, and when the membrane is used to separate concentrated solutions, the values of E_m are -ve, i.e., and the membrane becomes anion selective. Such reversal in selectivity character is not peculiar to these systems (25).

Two important factors, which control electrolyte permeability through a membrane, are charge on the membrane and its porosity. Parchment paper,

except for the presence of some stray and end carboxylic group, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on membrane surface in the dilute solutions of a 1:1 electrolyte leading to the type of ionic distribution associated with the electrical double layer (34). The stepwise change in membrane potential or the selectivity character of the membrane-electrolyte system may readily be explained in terms of the structural changes produced in the electrical double layer at the interfaces parchment supported nickel and cobalt phosphate membranes are considered negatively charged in contact with water. It is probable that in these cases the negative charge is due to the firm attachment of hydroxyl ions from the water and/or PO_4^{3-} ions from the solution. Constituting the membrane. An equivalent number of protons and/or cations, some closely held in the fixed part of the double layer and the remainder in the diffuse portion, will be left in the solution. By the addition of univalent electrolytes, there will be a tendency for the cations to accumulate on the solution side of the fixed double layer. By increasing the positive charge density, the interfacial potential difference changes thereby changing the overall membrane potential if the electrolyte. Concentration is made large the sign of the electrical potential may eventually be reversed leading to a state where the membrane becomes anion selective Fig. 3 depicts a family of hypothetical potential profiles existing across the cobalt and nickel phosphate membranes.

The fixed groups present in well-characterized ion exchange membranes can be easily estimated by titration. This procedure was used by

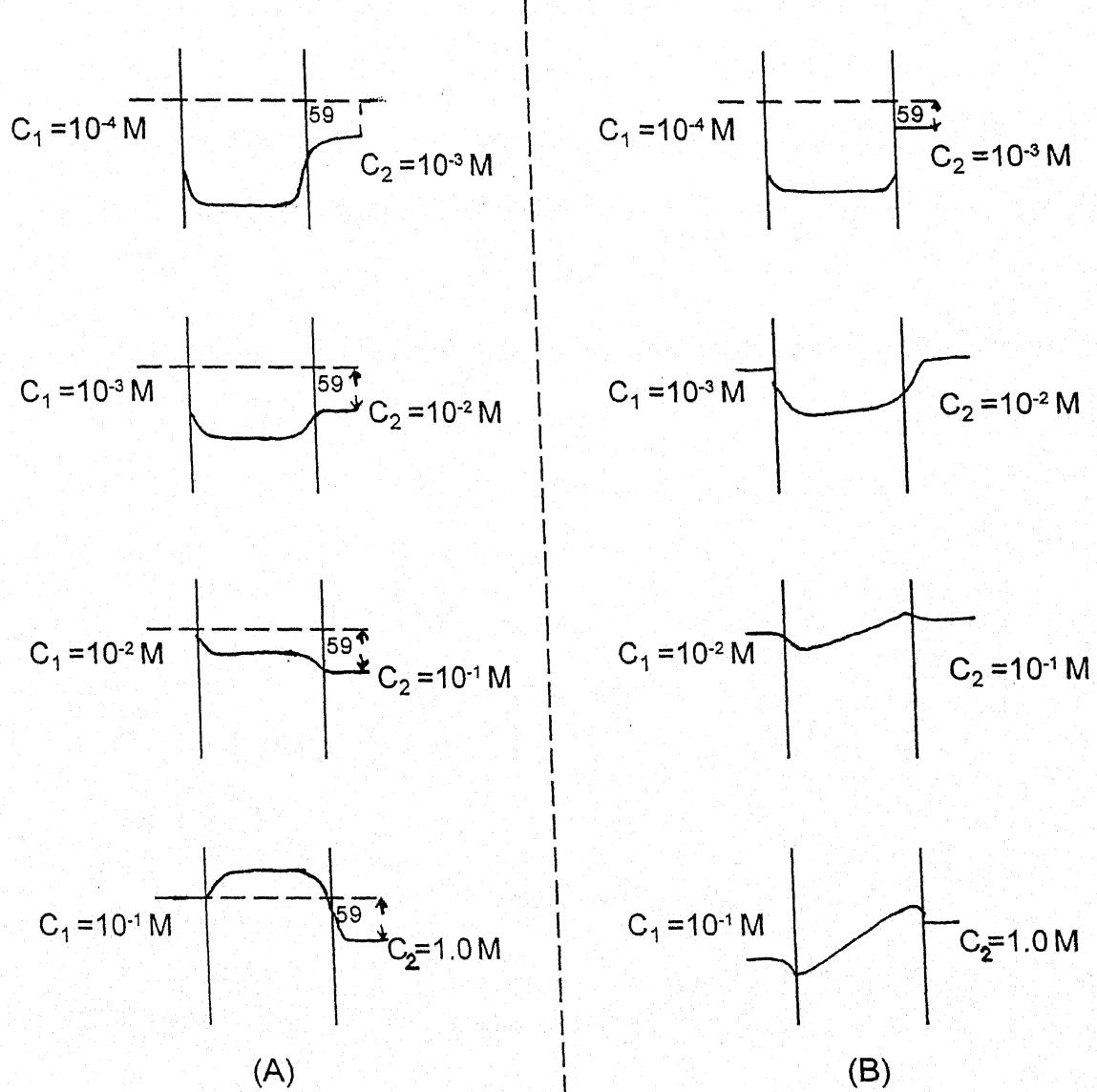


FIG • 3

(A,B) HYPOTHETICAL POTENTIAL PROFILES EXISTING ACROSS
THE MEMBRANES,

Sollner et al. (35) to estimate the end groups and stray carboxylic groups present in the collodion material. Lakshminarayanaiah (36) in his studies with thin membrane of parlodion, used two methods – the isotopic and the potentiometric to evaluate the apparent fixed charge on the membrane material. In the present studies the titration method proved inconvenient and very inaccurate, while the isotopic method was discarded in view of the strong ionic adsorption phenomena exhibited by these systems. Consequently the potentiometric method was used. This method is based on the fixed charge theory of membrane potential proposed simultaneously by Teorell (2,3), and Meyer and Sievers (37). The fixed charge concept of Teorell (2,3) and Meyer and Sievers (37) (the TMS theory) for charged membranes is a pertinent starting point for the investigation of the actual mechanisms of the ionic or molecular processes, which occur in the membrane phase. According to this theory membrane potential is considered to be composed of two Donnan potential at the two solution membrane interfaces and a diffusion potential arising from unequal concentration of the two membrane phases. These authors derived following equation for membrane potential in millivolts (at 25° C) applicable to a highly idealized system, viz:

$$E_m = 59.2 \left[\log \frac{C_2 \left(\sqrt{4C_1^2 + \bar{X}^2} + \bar{X} \right)}{C_1 \left(\sqrt{4C_2^2 + \bar{X}^2} + \bar{X} \right)} + \bar{U} \log \frac{\left(\sqrt{4C_2^2 + \bar{X}^2} + \bar{X}U \right)}{\left(\sqrt{4C_1^2 + \bar{X}^2} + \bar{X}U \right)} \right] \quad (2)$$

here $\bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v})$, \bar{u} and \bar{v} are the mobilities of cation and anion respectively in the membrane phase; \bar{X} is charge on the membrane expressed in equivalents/liter of imbibed solution. Equation (2) has been frequently used for the evaluation of the fixed charge density \bar{X} of a membrane (38). In order to evaluate this parameter for the simple case of 1:1 electrolyte and membrane carrying a net negative charge of unity ($\bar{X} = 1$), theoretical concentration potentials E_m existing across the membrane are calculated as function C_2 , are given in Table 3. The ratio C_2/C_1 being kept at constant value for different mobility ratios, \bar{u}/\bar{v} . The observed membrane potential values are then plotted in the same graph as a function of $\log(1/C_2)$. The experimental curve is shifted horizontally until it coincides with one of the theoretical curves. The extent of this shift gives $\log \bar{X}$ and the coinciding theoretical curve, the value of \bar{u}/\bar{v} , Figs. (4 and 5). In the case of cobalt and nickel phosphate membranes the observed membrane potential curves on shifting horizontally did not overlap with any of the theoretical curves particularly in the dilute ranges. As a result eq. (2) was used in another way, in the way Teorell did, to evaluate \bar{X} . A family of theoretical curves (Figs. 4 and 5) were constructed assigning $\bar{X} = 1$ and successively decreasing values to \bar{X} ($\bar{X} < 1$) keeping $\bar{u}/\bar{v} = 0.2$ (Table 5). The curves thus obtained have same shape and limit but are transposed along the $\log C_2$ axis. The value of \bar{X} is then given by the curve with which the experimental curve coincided. The values thus derived are given in Table 4. In addition to the value of \bar{X} , the plotting in this form correctly predicts diffusion potential at the limit $\bar{X} = 0$. The diffusion potential values derived in this way were

TABLE-3

Theoretical Values of Membranes E_m (mv) Calculated From Teorell-Meyer-Seivers Method For Different Mobility Ratio \bar{u}/\bar{v} and ($\bar{x}=1$) At Different Concentrations.

Mobility ration Concentration	C_2/C_1 (Mol/l)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
$1 \times 10^{-1}/1$		-35.0	-22.5	-3.0	8.3	15.3	16.1	20.2	23.5
$5/5 \times 10^{-1}$		-22.5	10.0	25.0	30.8	40.7	20.1	30.2	30.0
$1/1 \times 10^{-1}$		15.0	30.0	45.2	46.0	45.0	34.0	37.5	45.2
$5 \times 10^{-1}/x 10^{-2}$		35.0	40.0	47.5	47.2	50.2	50.0	53.0	55.0
$1 \times 10^{-1}/1 \times 10^{-2}$		50.0	50.0	50.0	55.5	55.0	55.0	57.0	58.8
$5 \times 10^{-1}/1 \times 10^{-2}$		58.0	57.0	55.0	58.0	59.0	59.2	59.4	60.0
$1 \times 10^{-1}/1 \times 10^{-2}$		59.0	59.0	59.0	59.0	59.9	59.9	60.0	60.0
$5 \times 10^{-1}/1 \times 10^{-2}$		60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
$1 \times 10^{-1}/1 \times 10^{-2}$		60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0

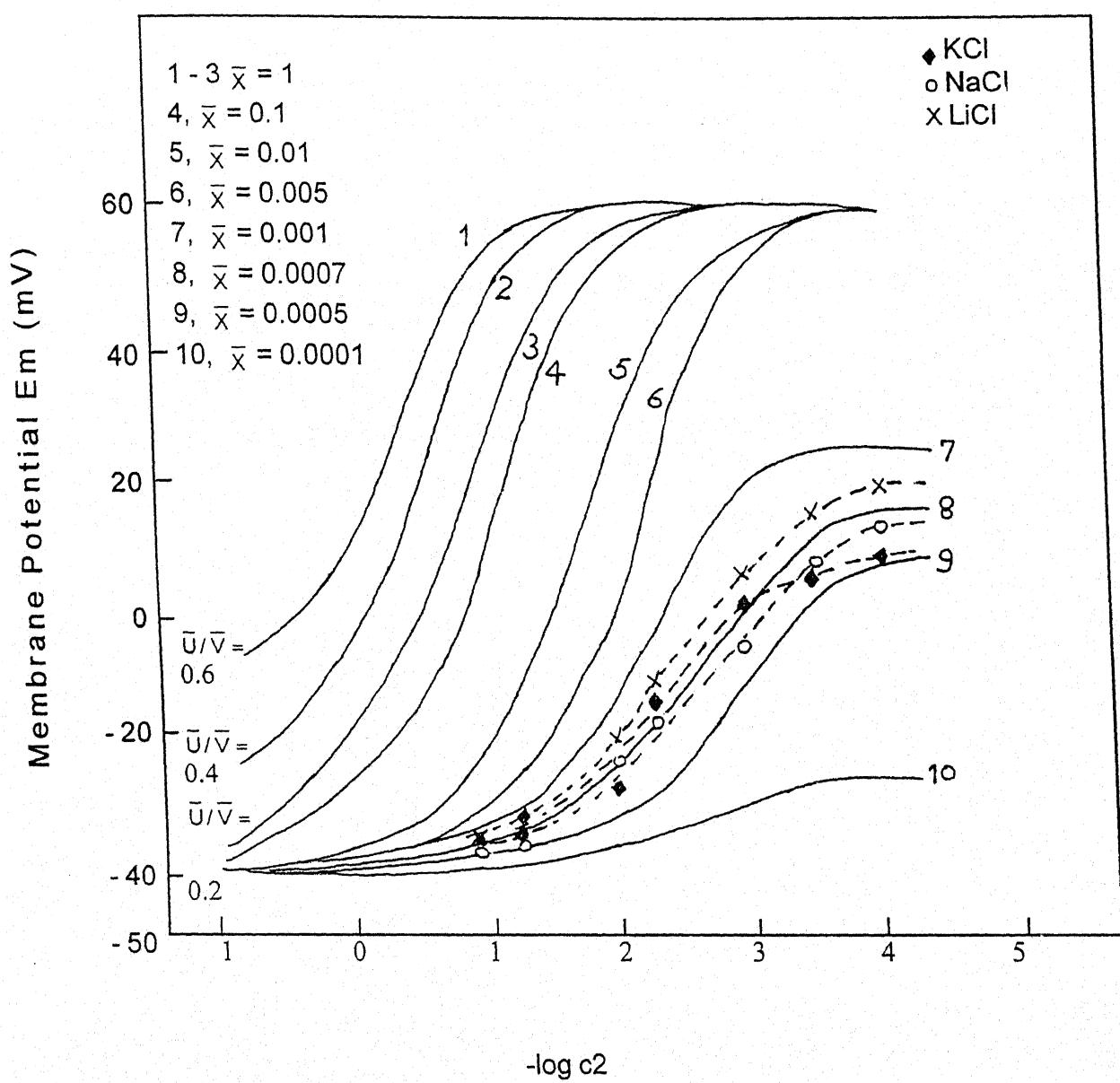


FIG. 4

SMOOTH CURVES ARE THE THEORETICAL CONCENTRATION POTENTIALS FOR
 $x = 1$ AND DIFFERENT MOBILITY RATIOS U/V , (1-3), AND $x = 1$ (4-10)
 FOR $\bar{U}/\bar{V} = 0.2$ BROKEN LINES ARE EXPERIMENTAL VALUES OF E_m (mV)
 FOR VARIOUS 1:1 ELECTROLYTES ACROSS COBALT PHOSPHATE MEMBRANE

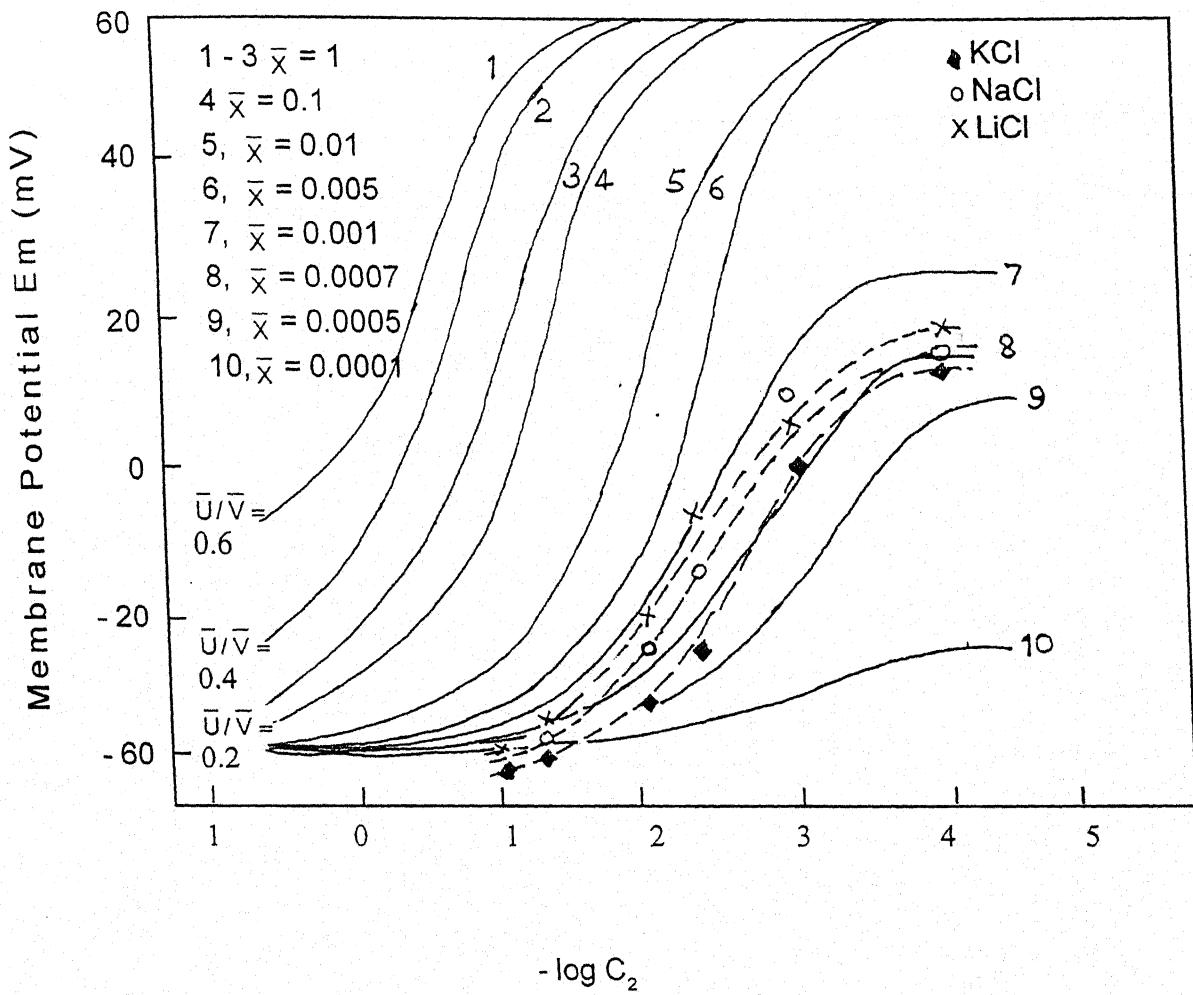


FIG. 5

SMOOTH CURVES ARE THEORETICAL CONCENTRATION POTENTIALS FOR
 $\bar{x} = 1$ AND DIFFERENT MOBILITY RATIOS \bar{U}/\bar{V} , (1 - 3) AND $\bar{x} < 1$ (4^{-10})
 FOR $\bar{U}/\bar{V} 0.2$ BROKEN LINES ARE EXPERIMENTAL VALUES OF E_m (mV)
 FOR VARIOUS 1:1 ELECTROLYTES ACROSS NICKEL PHOSPHATE MEMBRANE

TABLE-4

Values of Membrane Charge Density X (eq/L), Mobility Ratio (U/V) And Diffusion Potential (mv) For Various Membrane Electrolyte System Using Teorell-Meyer-Sievers Theory At $25 \pm 0.1^{\circ}\text{C}$

Electrolyte		KCl	NaCl	LiCl
Membranes	Parameters			
Cobalt phosphate	(X) $\times 10^3$	1.6	1.9	2.9
	(u/v)	0.2	0.2	0.2
	(Diff. Pot.)	-34.3	-38.6	-35.0
Nickel phosphate	(X) $\times 10^3$	1.8	1.4	2.5
	(u/v)	0.2	0.2	0.2
	(Diff. Pot.)	-42.4	-42.3	-40.5

TABLE-5

Theoretical Values of Membranes E_m (mv) Calculated From Teorell-Meyer-Sievers Method For Different Values of \bar{X} and $\bar{u}/\bar{v} = 0.2$.

Charge Density (\bar{X}) Concentration C_2/C_1 (Mol/l)	0.1	0.01	0.005	0.001	1.0007	1.0005	1.0001
1x10 ⁻¹ /1	-39.1	-39.5	-39.1	-39.1	-39.1	-39.8	-39.1
5/5x10 ⁻¹	-39.1	-39.7	-39.1	-39.1	-39.1	-39.8	-39.1
1/1x10 ⁻¹	-21.9	-37.3	-38.2	-38.2	-39.0	-39.0	-39.0
5x10 ⁻¹ /x10 ⁻²	-8.1	-36.4	-36.8	-36.2	-37.8	-39.0	-39.1
1x10 ⁻¹ /1x10 ⁻²	31.1	-30.7	-33.7	-35.2	-34.8	-37.5	-38.0
5x10 ⁻¹ /1x10 ⁻²	50.3	-2.2	-10.5	-30.7	-24.3	-28.5	-37.4
1x10 ⁻¹ /1x10 ⁻²	59.2	21.5	21.8	10.5	-10.0	-22.0	-30.0
5x10 ⁻¹ /1x10 ⁻²	59.5	41.3	54.7	21.9	9.1	-20.0	26.9
1x10 ⁻¹ /1x10 ⁻²	59.5	59.5	58.0	24.5	15.2	-19.5	-25.5

found to have approximately the same magnitude and sign as the potential across the membranes when these are used to separate highly concentrated solutions of an electrolyte (Table 4). In view of this limiting diffusion potential value, the variation in membrane potential across cobalt and nickel phosphate membranes with the change in external electrolyte concentrations may be ascribed to be due to the structural changes produced in the electrical double layer at the membrane- solution interfaces. Thus cobalt and nickel phosphate membrane electrolyte systems may be more conveniently described as consisting of two mini cells - one with constant e.m.f. corresponding to the limiting diffusion potential and the other with variable e.m.f. representing the international potential difference (0 to 60 mV approximately). Since the total membrane potential changes sign as the concentration of the electrolytes across the membranes are changed, thus it may be concluded that these mini cells are combined together in series but operating in opposite direction and that the membrane solution interface seems to be the rate determining step as suggested by Tien and Ting (39) for bilayer membranes.

Kobatake et al. (12) on the basis of the thermodynamics of irreversible processes derived the following equation for the electrical potential E_m which arises when a negatively charged membrane separates two solutions of a 1:1 electrolyte of concentrations C_1 and C_2 ($C_1 < C_2$):

$$E_m = - \frac{RT}{F} \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - \left(1 + \frac{1}{\beta} - 2\alpha \right) \ln \left(\frac{C_2 + \alpha\beta \bar{X}}{C_1 + \alpha\beta \bar{X}} \right) \right] \quad (3)$$

Where $\alpha = U / (u + v)$

$$\beta = 1 + KF \bar{X} / u$$

F and K represent, respectively, the Faraday constant and a constant dependent upon the viscosity of the solution and structural details of the polymer network of which the membrane is composed. To evaluate the membrane parameters, α , β and \bar{X} , two limiting forms of the above equation were derived. When the external salt concentration C is sufficiently small,

$$|E_m^\sigma| = \frac{1}{\beta} \ln \gamma - \left(\frac{\gamma - 1}{\alpha \beta \gamma} \right) \left(1 + \frac{1}{\beta} - 2\alpha \right) \left(\frac{C_2}{\bar{X}} \right) + \dots \quad (4)$$

$$\text{where } |E_m^\sigma| = FE_m / RT$$

$$\text{and } \gamma = C_2/C_1$$

when the salt concentration C is high,

$$\frac{1}{t_-} = \frac{1}{1 - \alpha} + \frac{(1 + \beta - 2\alpha\beta)(\gamma - 1)\alpha}{2(1 - \alpha)^2 \ln \gamma} \left(\frac{\bar{X}}{C_2} \right) + \dots \quad (5)$$

where t_- is the apparent transference number of coins (anions) in a negatively charged membrane defined by

$$E_m = (1 - 2t_-) \ln \gamma \quad (6)$$

The value of t_- calculated from observed membrane potentials using eq. (6) for cobalt and nickel phosphate membranes, are given in Tables 6 and 7.

Equation (4) was used to give the value of β (see Table 8) and a relation

between α and \bar{X} by evaluating the intercept and the initial slope of the plot of E_m against C_2 (Figs. 6 and 7), while eq. (5) was used to evaluate α (see Table 8) from the intercept of a plot of $1/t$ against $1/C_2$ (Figs. 8 and 9). The values of \bar{X} were determined by inserting this value of α in the relation between α and \bar{X} obtained earlier. The values of \bar{X} derived in this way for the membranes and 1:1 electrolytes are given in Table 9.

Once the values of the parameters α , β and \bar{X} for a given membrane-electrolyte system have been determined one can get the theoretical E_m Vs. C_2 curve using eq. (3) for any given γ ($=C_2/C_1$) and compare it with the corresponding experimental data. For this comparison eq. (3) can be rewritten in the following form as suggested by Kobatake and coworkers (12).

$$\frac{(\gamma - e^q)}{(e^q - 1)} = Z \quad (7)$$

with q and Z defined by

$$q = \frac{\left| E_m \right| + (1 - 2\alpha) \ln \gamma}{1/\beta + (1 - 2\alpha)} .$$

and $Z = C_2 / \alpha \beta \bar{X}$. Thus if eq. (7) is valid the value of $(\gamma - e^q)/(e^q - 1)$ calculated from the measured E_m with predetermined α , β and \bar{X} and the given value of γ must fall on a straight line which has a unit slope and passes the co-ordinate

TABLE-6

Transference Number ($t_{\text{--}}$) of Coins From Observed Membrane Potential At Various Electrolyte Concentration Through Cobalt Phosphate Membrane

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (mol/l)			
$1 \times 10^{-1}/1 \times 10^{-2}$	0.78	0.82	0.81
$5 \times 10^{-2}/5 \times 10^{-3}$	0.75	0.80	0.77
$1 \times 10^{-2}/1 \times 10^{-3}$	0.74	0.68	0.63
$5 \times 10^{-3}/5 \times 10^{-4}$	0.60	0.62	0.58
$1 \times 10^{-3}/1 \times 10^{-4}$	0.49	0.54	0.45
$5 \times 10^{-4}/5 \times 10^{-5}$	0.42	0.41	0.37
$1 \times 10^{-4}/1 \times 10^{-5}$	0.41	0.37	0.33

TABLE-7

Transference Number $t_{\text{--}}$ of Coins From Observed Membrane Potential At Various Electrolyte Concentration Through Nickel Phosphate Membrane

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (mol/l)			
$1 \times 10^{-1}/1 \times 10^{-2}$	0.85	0.85	0.84
$5 \times 10^{-2}/5 \times 10^{-3}$	0.83	0.84	0.82
$1 \times 10^{-2}/1 \times 10^{-3}$	0.76	0.70	0.76
$5 \times 10^{-3}/5 \times 10^{-4}$	0.62	0.60	0.55
$1 \times 10^{-3}/1 \times 10^{-4}$	0.46	0.42	0.46
$5 \times 10^{-4}/5 \times 10^{-5}$	0.41	0.41	0.43
$1 \times 10^{-4}/1 \times 10^{-5}$	0.39	0.34	0.37

TABLE-8

Values of the Membrane Parameter α and β for Various Membrane Electrolyte At $\gamma = 10$

Electrolyte Membranes	KCl		NaCl		LiCl	
	α	β	α	β	α	β
Cobalt	0.18	1.2	0.17	1.2	0.16	1.2
Phosphate						
Nickel	0.11	1.5	0.13	1.5	0.14	1.5
Phosphate						

TABLE-9

Values of The Effective Fixed Charge Density \bar{X} (eq/l) Using Kobatake's Method For Various Membrane Electrolyte System At $25 \pm 0.1^\circ\text{C}$

Electrolyte Membranes	KCl	NaCl	LiCl
Cobalt phosphate			
$(\bar{X}) \times 10^3$, eq/l	5.3	2.5	3.7
Nickel phosphate			
$(\bar{X}) \times 10^3$, eq/l	1.9	4.7	4.2

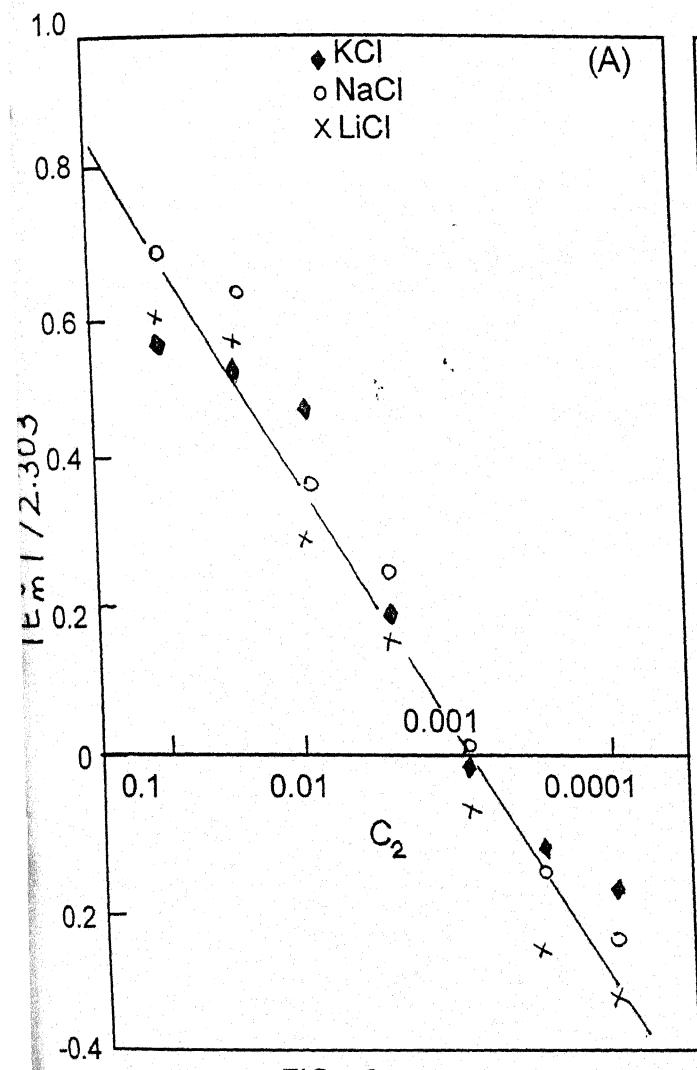


FIG. 6

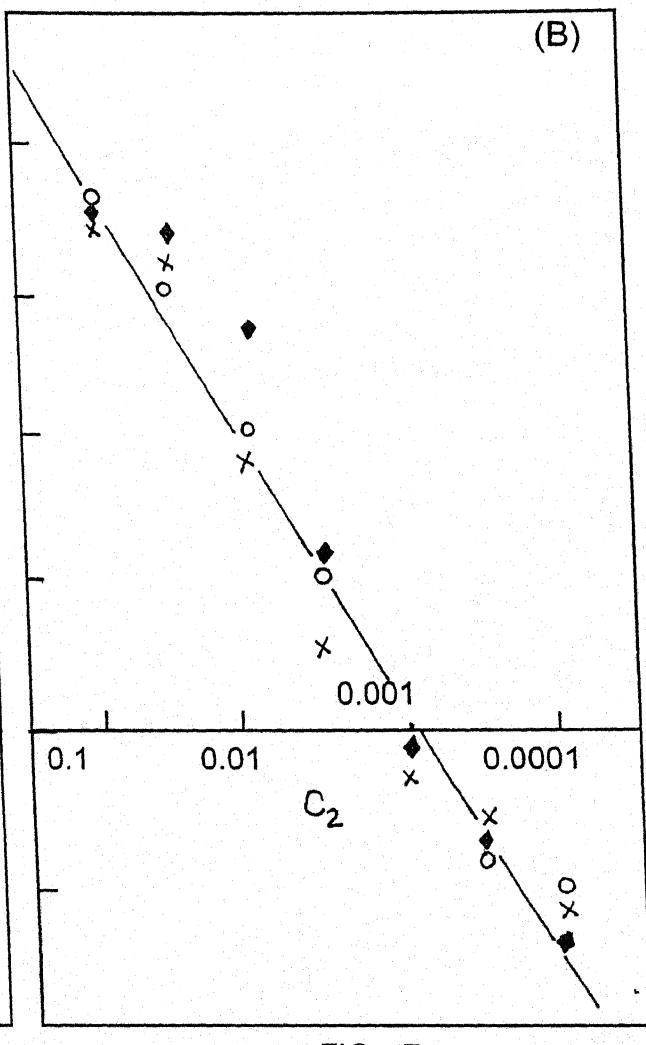


FIG. 7

PLOTS OF $|E_m|/2.303$ AGAINST C_2 FOR (A) COBALT PHOSPHATE AND (B) NICKEL PHOSPHATE MEMBRANES IN CONTACT WITH VARIOUS 1:1 ELECTROLYTE SOLUTIONS

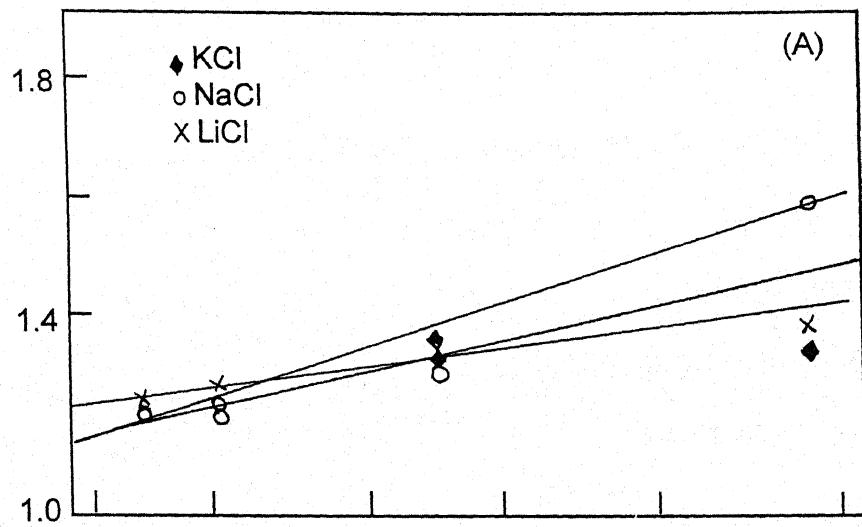


FIG. 8

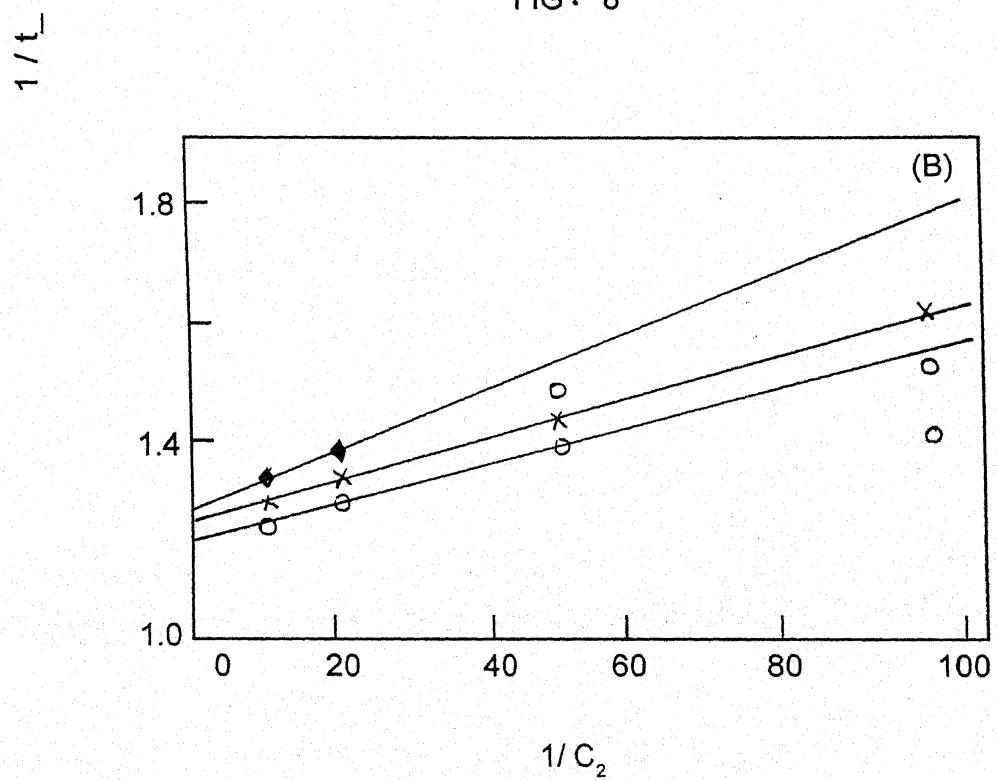


FIG. 9

PLOTS OF $1/t$ - AGAINST $1/C_2$ FOR (A) COBALT PHOSPHATE AND (B)
NICKEL PHOSPHATE MEMBRANES USING
1:1 ELECTROLYTE SOLUTIONS
AT CONSTANT γ ($\gamma = 10$)

origin when plotted against Z . This behavior should be observed irrespective of the value of γ and the kind of membrane-electrolyte system used.

Recently Kobatake and Kamo (17) derived another equation eq. (8) for the membrane potential starting with the basic flow equation provided by the thermodynamics of irreversible processes and using a different set of assumptions: namely, (a) the contribution of mass movement is negligible (17), and (b) small ions do not behave ideally in a charged membrane (17).

Their result is:

$$E_m = -\frac{RT}{F} \left[\ln \frac{C_2}{C_1} + (2\alpha - 1) \ln \frac{\sqrt{4C_2^2 + \phi^2 X^2} + (2\alpha -)\phi X}{\sqrt{4C_1^2 + \phi^2 X^2} + (2\alpha -)\phi X} - \ln \frac{\sqrt{4C_2^2 + \phi^2 X^2} + \phi X}{\sqrt{4C_1^2 + \phi^2 X^2} + \phi X} \right] \quad (8)$$

where ϕ is a characteristic factor of the membrane-electrolyte pair, and represents the fraction of counter ions not tightly bound to the membrane skeleton. The product ϕX is termed the thermodynamically effective fixed charge density of a membrane; the other terms have their usual significance. Equation (8) reduces to the TMS membrane potential for $\phi = 1$. Since it is somewhat troublesome to evaluate ϕX at an arbitrary external electrolyte concentration from the observed membrane potential using eq. (8), Kobatake and Kamo (17) have proposed a simple method using the following approximate equation for the diffusive contribution to the e.m.f. of a cell with transport:

$$E_m = -\frac{RT}{F} (1 - 2t_{app}) \ln (C_2/C_1) \quad (9)$$

where t_{app} is the apparent transference number of ions in the membrane phase. Comparison of eqs. (8) and (9) gives

$$t_{app} = \frac{1-2\alpha}{2} \frac{\ln\left(\frac{\sqrt{4\xi_2^2 + 1 + 2\alpha - 1}}{\sqrt{4\xi_1^2 + 1 + 2\alpha - 1}}\right)}{\ln \gamma} + \frac{\ln\left(\frac{\sqrt{4\xi_2^2 + 1 + 1}}{\sqrt{4\xi_1^2 + 1 + 1}}\right)}{2\ln \gamma} \quad (10)$$

where $\xi = C/\phi X$

on the other hand (16,17), the mass fixed transference number of ions in a negatively charged membrane immersed in an electrolyte solution of concentration C was defined by

$$t_- = v \bar{C}_- / (u \bar{C}_+ + v \bar{C}_-) \quad (11)$$

where \bar{C}_+ and \bar{C}_- are the concentrations of cation and anion, respectively, in the membrane phase. This equation was transformed to

$$t_- = 1 - \alpha \frac{\sqrt{4\xi^2 + 1 + 1}}{\sqrt{4\xi^2 + 1 + (2\alpha - 1)}} \quad (12)$$

using certain equations for the activity coefficients, mobilities of small ions in the membrane phase, and the equilibrium condition for electrical neutrality (16,17). The difference between the apparent transference number t_{app} calculated from eq. (10) and t_- from eq. (12) for various reduced concentrations ξ ($\xi = C/\phi X$) was found to be always less than 2% over a

wide range of external electrolyte concentrations. Therefore, t_{app} and t_- were considered practically the same. As a result, the apparent transference number evaluated from the membrane potential data used for the determination of the thermodynamically effective fixed charge density σX of the membrane at a given average salt concentration C ($C = (C_1 + C_2)/2$) using eq. (12) At the same time rearrangement of eq. (12) provides a definition of perm selectivity P_s , given by the expression

$$\frac{1}{(4\xi^2 + 1)^{1/2}} = \frac{1 - t_- - \alpha}{\alpha - (2\alpha - 1)(1 - t_-)} = P_s \quad (13)$$

This equation can be used to find the perm selectivity from membrane potential measurements using eq. (9) If the transport number of cations (t_+ or t_{app}) is zero, the membrane is perfectly selective and $P_s = 1$, while if the transport number of cations has the value in free solution $P_s = 0$. The values of P_s obtained in Tables (10 and 11) using the right hand side of eq. (13) were plotted against $\log C$. The concentration at which P_s (where $\xi = C/\sigma X = 1$) becomes $(1/5)^{1/2}$ gives the value of the thermodynamically effective fixed charge density σX as required by the left side of eq. (13). Figures 10 and 11 represent plots of P_s versus $\log (C_1 + C_2)/2$ for the parchment supported cobalt and nickel phosphate membranes in contact with various 1:1 electrolytes. The value of σX thus derived for the membranes and 1:1 electrolyte combinations are given in Table 12.

More recently, Tasaka et al. (21) derived an equation for the membrane potential existing across a charged membrane. The total membrane potential E_m was considered as the sum of a diffusion potential E_d

TABLE-10

Values of Perm-selectivity P_s of The Membrane Using Various 1:1 Electrolytes At Different Concentration For Cobalt Phosphate Membrane

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (mol/l)			
$1 \times 10^{-1}/1 \times 10^{-2}$	0.56	0.75	0.77
$5 \times 10^{-2}/5 \times 10^{-3}$	0.50	0.71	0.70
$1 \times 10^{-2}/1 \times 10^{-3}$	0.48	0.53	0.49
$5 \times 10^{-3}/5 \times 10^{-4}$	0.20	0.42	0.43
$1 \times 10^{-3}/1 \times 10^{-4}$	-0.20	0.30	0.19
$5 \times 10^{-4}/5 \times 10^{-5}$	-0.16	-0.02	0.00
$1 \times 10^{-4}/1 \times 10^{-5}$	-0.18	-0.07	-0.10

TABLE-11

Values of Perm-selectivity P_s of The Membrane Using Various 1:1 Electrolytes at Different Concentration For Nickel Phosphate Membrane

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (mol/l)			
$1 \times 10^{-1}/1 \times 10^{-2}$	0.70	0.79	0.84
$5 \times 10^{-2}/5 \times 10^{-3}$	0.66	0.78	0.77
$1 \times 10^{-2}/1 \times 10^{-3}$	0.52	0.54	0.69
$5 \times 10^{-3}/5 \times 10^{-4}$	0.24	0.39	0.35
$1 \times 10^{-3}/1 \times 10^{-4}$	-0.12	0.05	0.19
$5 \times 10^{-4}/5 \times 10^{-5}$	-0.18	0.02	0.12
$1 \times 10^{-4}/1 \times 10^{-5}$	0.022	-0.13	0.00

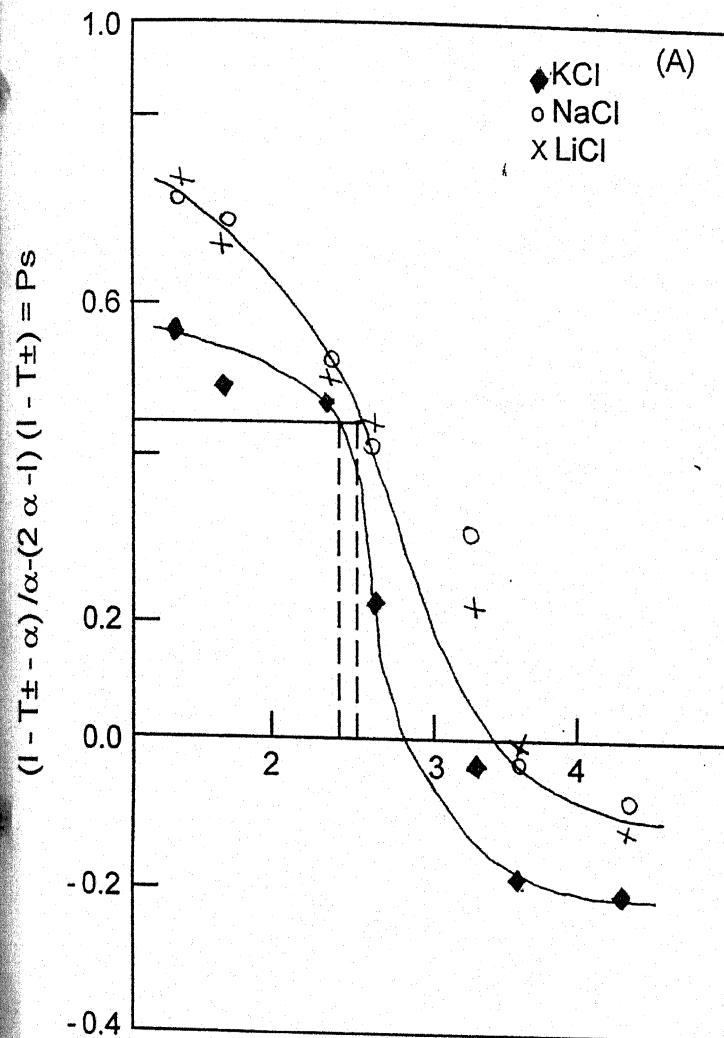


FIG 10

$$-\log (C_1 + C_2) / 2$$

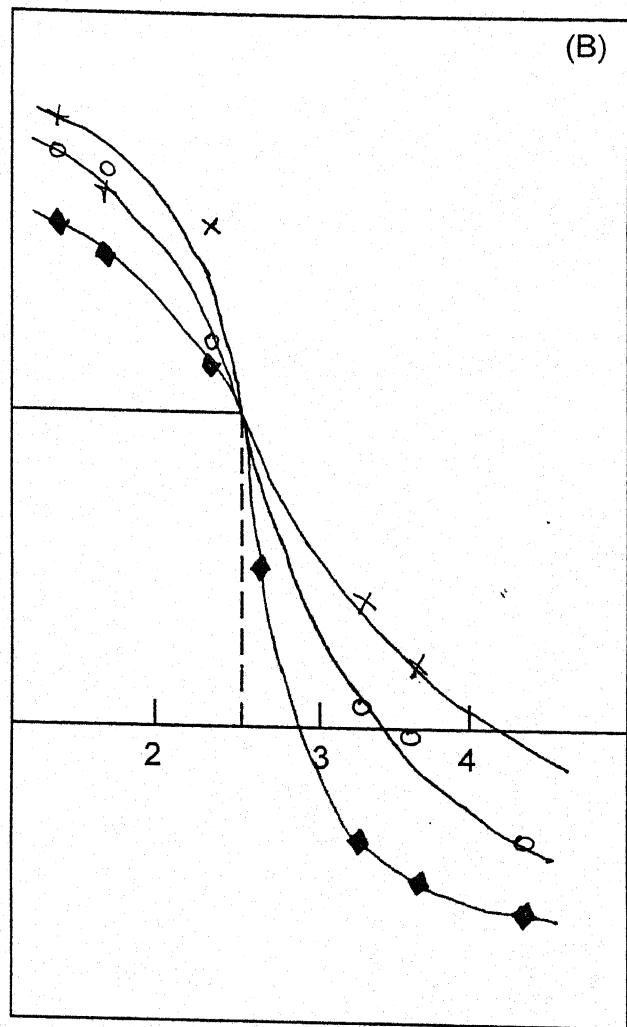


FIG 11

PLOTS OF Ps AGAINST $-\log (C_1 + C_2) / 2$ FOR (A) COBALT PHOSPHATE AND (B) NICKEL PHOSPHATE MEMBRANES

inside the membrane and the electrostatic potential differences E_e between the membrane surfaces and the electrolyte solutions on both sides of the membrane. The diffusion potential E_d was obtained by integrating the basic flow equation for diffusion (39), while the electrostatic potential difference was calculated from the Donnan's theory. Stated mathematically,

$$E_m = E_d + E_e \quad (14a)$$

where

$$\begin{aligned} -E_d = & - \int_1^2 \frac{J_0}{F \bar{C}_0} \frac{\phi X}{(\bar{C}_- + \phi X) u + \bar{C}_- v} dx + \\ & \frac{RT}{F} \int_1^2 \frac{(\bar{C}_- + \phi X) u}{(\bar{C}_- + \phi X) u + \bar{C}_- v} d \ln \bar{a}_+ - \\ & \frac{RT}{F} \int_1^2 \frac{\bar{C}_- v}{(\bar{C}_- + \phi X) u + \bar{C}_- v} d \ln \bar{a}_- \end{aligned} \quad (14b)$$

and

$$-E_e = - \frac{RT}{F} \ln \left(\frac{\bar{a}_1 \bar{a}_2}{\bar{a}_1 \bar{a}_2} \right) \quad (14c)$$

where a_1 and a_2 are the activities of the electrolytes on the two sides of the membrane, the overbar refers to the phenomena in the membrane phase. J_0 is the flow of electrolyte in the absence of an external electrolyte field, the other symbol have their usual significance. On integrating eq. (14) in the limit of high electrolyte concentrations across the membrane, one obtains the following equation for the membrane potential:

$$\begin{aligned}
 -E_m = & \frac{RT}{F} \left(\frac{\phi X}{2} \right) \left(\frac{\gamma - 1}{\gamma} \right) \frac{1}{C_2} + \frac{RT}{F} \left(\frac{u - v}{u + v} \right) \left[\frac{1 - \frac{\phi X J_o}{RT C_o (u - v) K}}{1 - \frac{\phi X J_o}{2RT C_o v K}} \right] \ln \gamma \\
 & + \frac{RT \phi X}{2Fuv} \left(\frac{J_o}{RT C_o K} \right)^2 \frac{\left[1 - \frac{\phi X J_o (u + v)}{4RT C_o u v K} \right]}{\left(1 - \frac{\phi X J_o}{2RT C_o v K} \right)^2} (\gamma - 1) C_2 \quad (15)
 \end{aligned}$$

At high electrolyte concentrations, eq. (15) can be approximated by

$$-E_m = \frac{RT}{F} \frac{(\gamma - 1)}{\gamma} \left(\frac{\phi X}{2} \right) \frac{1}{C_2} + \dots \quad (16)$$

Equation (16) predicts a linear relationship between E_m and $1/C_2$ from which ϕX can be calculated. Plots of E_m versus $1/C_2$ for the membranes are represented in Figs. 12 and 13. Sets of straight lines in agreement with eq. (16) are obtained. The values of ϕX derived from the slopes of the lines are given in Table 13.

It is noted from Tables 5, 9, 12 and 13 that the charge densities of the membrane electrolyte system are low. This is in accordance with our earlier findings of diffusion rate studies. Further, the values derived from different methods are almost the same. A little difference may be attributed to the different procedures adopted. It is concluded, therefore, that the methods developed recently by Kobatake et al. and Tasaka et al. for the evaluation of effective fixed charge density are valid for the systems under investigation.

TABLE-12

Values of Effective Fixed Charge Density ϕX (eq/l) Obtained From Kobatake's Perm-selectivity Method For Various Membrane Electrolyte Systems At $25 \pm 0.1^\circ\text{C}$

Electrolyte Membranes	KCl	NaCl	LiCl
Cobalt phosphate (ϕX) $\times 10^3$, eq/l	4.5	3.2	3.2
Nickel phosphate (ϕX) $\times 10^3$, eq/l	3.2	3.2	3.2

TABLE-13

Values Of Effective Fixed Charge Density ϕX (eq/l) Obtained From Tasaka's Method For Various Membrane Electrolyte System At $25 \pm 0.1^\circ\text{C}$

Electrolyte Membranes	KCl	NaCl	LiCl
Cobalt phosphate (ϕX) $\times 10^3$, eq/l	1.1	1.7	2.0
Nickel phosphate (ϕX) $\times 10^3$, eq/l	1.1	2.0	2.2

Membrane Potential E_m (mV)

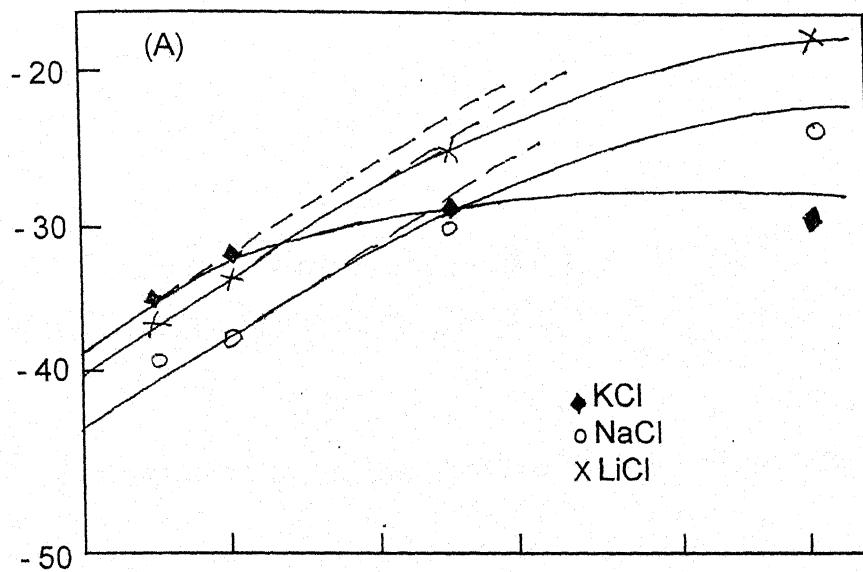


FIG . 12

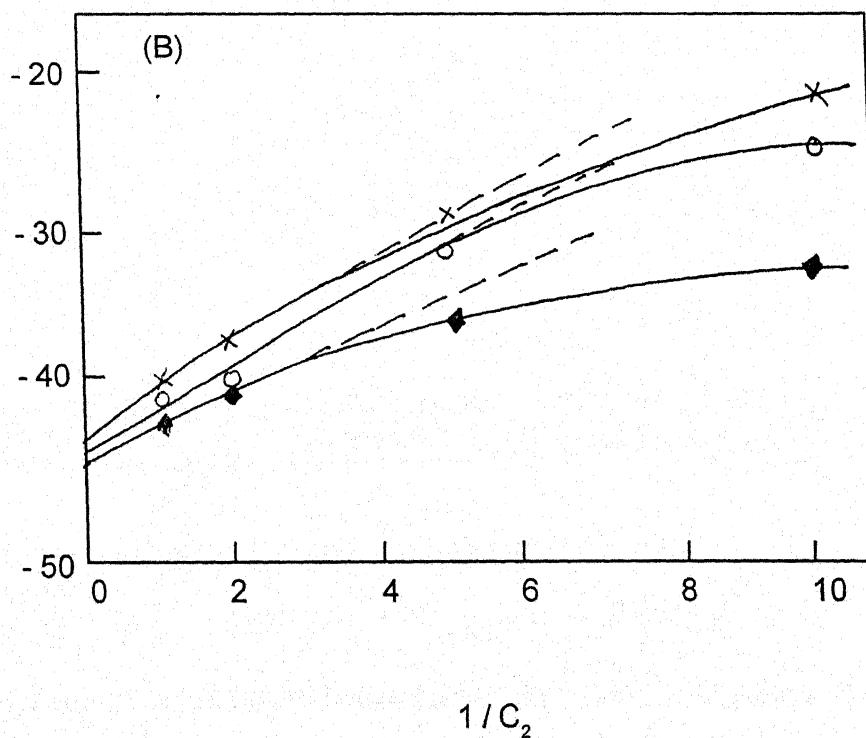


FIG . 13

PLOTS OF MEMBRANE E_m (mV) AGAINST $1/C_2$ FOR (A) COBALT PHOSPHATE AND (B) NICKEL PHOSPHATE MEMBRANES

REFERENCES

1. M. Goldsmith, D. Har, and R. Damadian, *J. Phys. Chem.*, 79, 342 (1975).
2. T. Teorell, *Proc. Soc. Expt. Biol.*, 33, 282 (1935); *J. Gen. Physiol.*, 19, 917 (1936); *Proc. Natl. Acad. Sci. (U.S.A.)*, 21, 152 (1935); *Z. Electrochem.*, 55, 460 (1951); *Nature*, 162, 961 (1948); *Arch. Sci. Physiol.*, 3, 205 (1949); *Prog. Biophys. Chem.*, 3, 385 (1953).
3. T. Teorell, *Discuss. Faraday Soc.*, No. 21, 9 (1956)
4. A.K. Chakarvarti, B. Christensen and P. langer, *J. Membrane Sci.*, 22, 111, (1985)
5. K. Singh, A.K. Tiwari and C.S. Dwivedi, *Ind. J. of Chemistry*, Vol. 39A, 495, (2000).
6. J. Benavente, A. Munoz, A. Heredia, A. Canas, *Colloids and Surfaces A. Physicochemical and Engineering*, Vol. - 159, 2, 423, (1999).
7. J. Schaep, C. Vande casteele, *J. Membrane Sci.*, 188, 129, (2001)
8. M.N. Beg and M.A. Matin, *J. Membrane Sci.*, 196, 95 (2002)
9. T. Ueda, N. Kamo, N Ishida, and Y. Kobatake, *J. Phys. Chem.*, 76, 2447 (1972).
10. M. Nagasawa and Y. Kobatake, *J. Phys. Chem.*, 56, 1017 (1952).
11. Y. Kobatake, *J. Chem. Phys.*, 28, 146 (1958).
12. Y. Kobatake, T. Noriaki, Y. Toyoshima, and H. Fujita, *J. Phys. Chem.*, 69, 3981 (1965).

13. N. Kamo, Y. Toyoshima, H. Nozaki, and Y. Kobatake, *Kolloid-Z, Z-Polym.*, 248, 948 (1971); 249, 1061 (1971).
14. Y. Toyoshima, M. Yuasa, Y. Kobatake, and H. Fujita, *Trans. Faraday Soc.*, 63, 2803, 2814 (1967).
15. M. Yuasa, Y. Kobatake, and H. Fujita, *J. Phys. Chem.*, 72, 2871 (1968).
16. N. Kamo, M. Oikawa, and Y. Kobatake, *J. Phys. Chem.*, 77, (1973).
17. Y. Kobatake, and N. Kamo, *Prog. Poly. Sci. Jpn.*, 5, 257 (1972).
18. T. Ueda and Y. Kobatake, *J. Phys. Chem.*, 77, 2995 (1973); N. Kamo, *Chem. Pharm. Bull. Jpn.*, 23, 3146 (1975).
19. N. Kamo, N. Nazemota, and Y. Kabatake, *Talenta*, 24, 111 (1977).
20. H. Fujita And Y. Kobatake, *J. Colloid. Interface Sci.*, 27, 609 (1968).
21. M. Tasaka, N. Aoki, Y. Konda, and, M. Nagasawa, *J. Phys. Chem.*, 79, 1307 (1975).
22. N. Lakshminarayanaiah, "Transport Phenomena In Membrane", Academic Press, New York, N.Y.P. 196 (1969).
23. F.A. Siddiqi, N. Lakshminarayanaiah, and M.N. Beg, *J. Polym. Sci.*, 9, 2869 (1971).
24. R.S. Kushwaha, M.A. Ansari, N. Akhtar and P. Singh, *Ind. J. of Chem.*, Vol. 31 A, 439 (1992).
25. M.A. Ansari, R.S. Kushwaha, A.K. Verma and C.M. Gupta, *U. Scientist, Phyl. Sciences*, Vol. 8, 1, 19, (1996).
26. R.S. Kushwaha, R. Tiwari, A. Gupta and M.A. Ansari, *Flora and Fauna*, 3, 1, (1997).

27. R.S. Kushwaha, H.P.S. Sengar, A. Gupta, R. Tiwari, and M.A. Ansari, *Flora and Fauna*, 4, 2, (1998).
28. R.S. Kushwaha, H.P.S. Sengar, A. Gupta, R. Tiwari and M.A. Ansari, *Flora and Fauna*, 4,2, 93, (1998).
29. R.S. Kushwaha, M.A. Ansari and R. Tiwari, *Ind. J. of Chem.*, Vol. 4A, 270 (2001).
30. R.S. Kushwaha, A. Kumar, R.B. Sharma and S. Agarwal, *Flora and Fauna*, 7, 9 (2001).
31. R.S. Kushwaha, M.A. Ansari and R. Tiwari, *Ind. J. of Chem.*, Vol. 40A, 270 (2001).
32. R.S. Kushwaha, M.A. Ansari, A. Bhartiya, *Chem. Environ. Res.*, 12, (3&4) 26, (2003).
33. R.S. Kushwaha, S. Agarwal and M.A. Ansari, *J. of the Ind. Council of Chemists*, Vol. 21, No. 2, 10, (2004).
34. N. Lakshminarayanaiah, "Transport Phenomena in Membranes", Academic Press, New York, P. 243 (1969).
35. K. Sollner, *J. Phys. Chem.*, 47, 171 (1945).
36. N. Lakshminarayanaiah and F.A. Siddiqi, *Biophys. J.*, 11, 600, 617 (1917); *Ibid*, 12, 540 (1972).
37. K.H. Meyer and J.F. Sievers, *Helv Chim. Acta.*, 19, 649, 665, 987 (1936).
38. N. Lakshminarayanaiah, "Transport Phenomena in Membranes", Academic Press, New York, P. 202-203 (1969).
39. H.T. Tien and H.P. Ting, *J. Colloid, Interfaces Sci.*, 27,702 (1968).

Chapter :II

*Diffusion
Rate of Metal
Ion Across the
Membrane*

INTRODUCTION

The transport of chemical species across synthetic and biological membranes is of great interest in many areas, ranging from, for example, separation (1) membrane supported reaction (2) and gas permeation (3) to life science application such as transmural drug delivery (4). In many cases transport measurements are averaged over the whole (or a large section of) the membrane. When correlation is made between the rate of transport and the structure of the membrane, the latter is often from ex Situ microscopy studies. Further more, the transport process is involved in the membranes as to use them as membrane distillation (M.D.). In fact it is a membrane process that has long been investigated. In small scale laboratory studies and the potential to become a viable tool for water desalination (5) M.D. is a separation process that combines simultaneous mass and heat transfer through a hydrophobic microporous membrane. The mass transfer in direct contact membrane distillation is three step process involving (i) diffusive transport from the feed stream to the membrane interface (ii) combined diffusive and convective transport of the vaporous through the membrane pores, and (iii) condensation of the vapour on the membrane interface on the product side of the membrane

When two electrolyte solutions having different concentrations are separated by a membrane, the mobile species penetrate the membrane and various transport phenomena are induced into the system. The number of forces that may normally operate in the absence of external magnetic and gravitational forces to cause a flow or flux of molecular or ionic species

through' it are': (I) difference of chemical potential $\Delta\mu$, (ii) difference of electric potential ΔE , (iii) difference of pressure ΔP , (iv) difference of temperature ΔT . These forces when operate individually or in combination may generate a number of phenomena (6-9). These are schematically represented in a recent book written by Lakshminarayanaiah (10). A prerequisite for the success of many operations indicated in the figure is the availability of suitable membrane system. Therefore, considerable attention has been given in recent years to the development of membranes ,with particular and predetermined specific properties. A variety of compound and associated processes that have been employed to prepare them and the important literature concerning transport phenomena are described in a number of books (11-15). A theoretical discussion of many of transport phenomena has been given in a monograph by Schlogl (16) and also appeared in the proceedings published in recent years '(17-21).

Transport processes occurring across membranes are of great interest for biologists, who use them as simple models for physiological membranes in order to understand, the behaviour of complex cell membranes in terms of established physicochemical principles. It was demonstrated by Teorcell (22) that the gastrict nucosal membrane, in some formal aspects at least behaved exactly like parchment membrane. His further findings that electrolytic transport processes in stomach could be handled by some thing similar to Fick's diffusion law and that Nernst Plank formulae for electrical potential were applicable who encouraged the studies of (a) the assymetric polymeric membranes (23-27) which mimic some of the properties of nerve cells (28,29) as models for biological system and (b) for us to proceed further with

the studies of parchment supported membranes (30-38).

Theories of membrane behaviour, particularly those of complex ions, have been discussed by Kedem and Katchalsky(39) in a series of theoretical papers. The various theories according to Schlogl(40) may be roughly divided into three groups, depending on the nature of the flux equation used in the treatment. Older theories or their modern refinements based on the Nernst-Planck flux equation fall into one group. A second group comprises the theories which use the principle of irreversible thermodynamics. The third group is made up of those theories which utilize the concepts of the theory of rate processes. These have been reviewed in a number of monographs, particularly that of Lakshminarayanaiah (10).

In this chapter, the diffusion rate studies of simple metal ions through parchment supported nickel and cobalt phosphate membranes under isothermal conditions are described. The diffusion rate of the ions have been computed using a simple cell assembly shown in Fig. 1. The advantage of the method is that various membrane parameters namely, membrane resistance R_m , membrane potential E_m and the computed diffusion rate could be known within two three minutes. The method is based on the equation derived by W.W. Kittelberger (48) from the simple laws of electrolysis. The results have been discussed in the light of Eisenman-Sherry model of membrane selectivity (41-43) and the theory of absolute reaction rates (44-46).

EXPERIMENTAL

Parchment supported cobalt and nickel phosphate membranes were prepared by the method of interaction suggested by Kushwaha and co-workers (30,

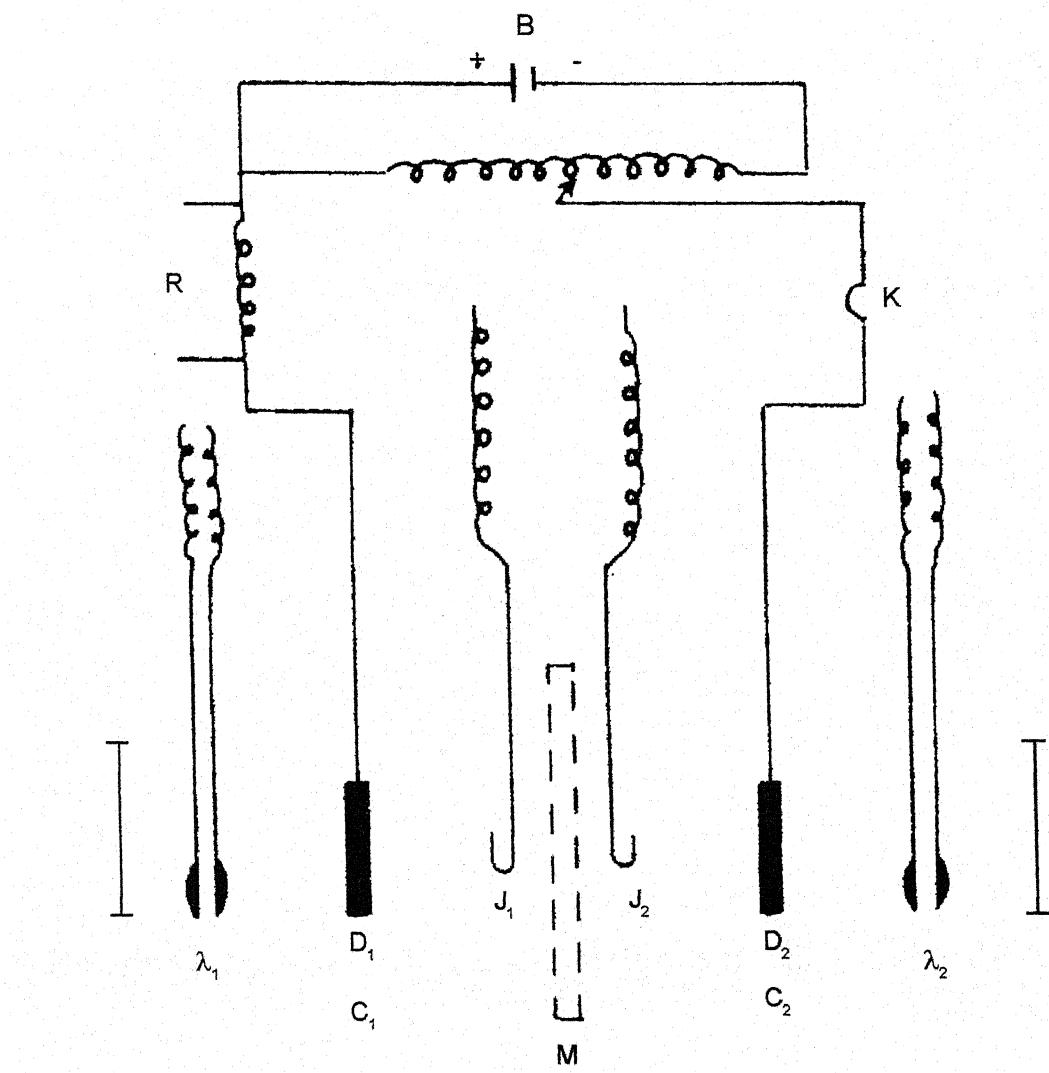


Fig. - 1

ASSEMBLY

31). To precipitate these substances in the interstices of parchment paper, a 0.2 M solution of sodium tri-orthophosphate was placed inside a glass tube, to one end of which was tied the parchment paper (supplied by M/s Baird and Tatlock London Ltd.) previously soaked in water. The tube was suspended for 72 hours in a 0.2 M solution of either cobalt (16) or nickel (16) chloride. The two solutions were interchanged later and kept for another 72 hours. The membranes thus prepared were washed with deionized water to remove free electrolytes. It was then clamped between two half cells as shown in Fig. 1. The half cells contained 125 ml of electrolyte solution while the capacity of each of the cell holding the membrane was about 130 ml. Initially these concentrations C_1 and C_2 were 0.001 M and 0.1 M. Each of the half cell was fitted with a conductivity cell (λ_1 and λ_2) firmly fitted to follow concentration changes using conductivity bridge (Cambridge Instrument Co., England. No. 350140) and two anion reversible Ag-AgCl electrodes one a disc type (D_1 , D_2) to pass a small D.C. current and another J-shaped wire electrode (J_1 , J_2) to measure membrane potential following current flow. The solutions in both the half cells were kept well stirred by magnetic stirrers. The whole cell assembly was immersed in a water thermostat maintained at 10°C , 15°C , 20°C and 25°C ($\pm 0.1^\circ\text{C}$)

Exactly known weights or volumes of test solutions were introduced (say at zero time) and the platinized platinum electrodes were connected to the conductivity bridge to follow conductance change with time. No appreciable change in conductance was noted within the 4 hr period on the C_2 side (0.1 M) and so we have assumed this concentration to be practically constant and followed only the conductance change on the C_1 side. The exact

concentration of this solution was determined from a calibration curve where conductance was plotted against concentration.

Another set of calibration curves were also needed to obtain concentration potential E_C^+ from the plots of e.m.f against $\log f_C$, according to the equation

$$E_C^+ = RT/z \cdot F \ln f_C \quad (1)$$

using a pair of saturated calomel and Ag-AgCl electrodes in the test solutions on either side of membrane. For all the electrolytes under investigation E_C^+ was taken as the difference between e.m.f. value of the dilute and concentrated solutions.

Membrane resistance was determined by measuring potential across J_1 and J_2 electrodes with and without applying an external e.m.f. to the disc electrodes. The change in potential was taken as ΔV_m . The current I passed through the membrane system was determined by measuring IR drop across a Precision Kilo-ohm resistor. The current was kept very low in order to minimise the ion transfer during the period (2-3 min.) required for each resistance measurements. The direction of current flow was reversed in each successive measurements.

Membrane potentials were evaluated from the electrical potential developed across J_1 and J_2 electrodes when no current was being passed. The total potential E_{obs} developed across J-shaped Ag/AgCl electrodes(J_1 and J_2) is the algebraic sum of electrode potential E_C and membrane potential E_m .

E_C was calculated by the equation

$$E_{\bar{C}} = RT/Z_{-}F \ln a_2/a_1 \quad (2)$$

and E_m was obtained by subtraction. The thickness of the membranes were as follows:

1. Cobalt phosphate membrane = 0.024 cm
2. Nickel phosphate membrane = 0.025 cm.

RESULTS AND DISCUSSION

Transport phenomena are often described by some extended form of the Nernst-Plank Flux equation (47). Evaluation of flow requires integration of these equations under suitable boundary conditions. Sometime ago, based on the simple laws of electrolysis, Kittelburger (48) developed the following equation for the migration of ions through a barrier

$$dQ/dt = \frac{1}{Z_{+}FR_m} \left[\frac{RT}{Z_{+}F} \ln \frac{a_2}{a_1} - E_m \right] \left[\left(\frac{Z_{-}}{Z_{+}Z_{-}} \right) \left(\frac{E_m}{RT/Z_{+}F \ln a_2/a_1} \right) + \left(\frac{Z_{+}}{Z_{+}+Z_{-}} \right) \right] \quad (3)$$

where a_1 and a_2 are the activities of the two solutions of an electrolyte on either side of the membrane, Q is the number of milliequivalents of ions diffusing in time t seconds, E_m is the membrane concentration potential, R_m is the electrolyte resistance of the membrane in ohms, Z_{+} , Z_{-} are the valency of cation and anion respectively, T is the absolute temperature, R is the gas const. and F is the Faraday const. Eq. (3) was used to give the rate dQ/dt at which various electrolysis diffuse through a membrane.

For electrolysis (1:1), equation (3) simplifies to

$$\frac{dQ}{dt} = \frac{1}{2FR_m} [(E_c^+ - E_m)] \left[\frac{Em}{E_c^+} + 1 \right] \quad (4)$$

For (2:1) electrolysis eq.(3) gives

$$\frac{dQ}{dt} = \frac{1}{3FR_m} \left[\left(\frac{E_c^+}{2} - Em \right) \right] \left[\left(\frac{Em}{E_c^+} + 1 \right) \right] \quad (5)$$

and for electrolytes of the type (3:1) it becomes.

$$\frac{dQ}{dt} = \frac{1}{4FR_m} \left[\left(\frac{E_c^+}{3} - Em \right) \right] \left[\left(\frac{Em}{E_c^+} + 1 \right) \right] \quad (6)$$

The values of membrane potential Em , membrane resistance R_m , and the diffusion rate dQ/dt derived from the experimental data and using eqs. (4-6) for both cobalt and nickel phosphate membranes in contact with different concentrations of various electrolytes are given in tables (1-30), and also depicted in Figs. 2-25 against the diffusion time while comparative values for various cations are shown in Figs. 26 and 27.

Tables 1-30 show that the membrane resistance R_m sequence for both the membranes at any given time for alkali metal ions is $Li^+ > Na^+ > K^+$; for alkaline earth metal ions is $Ba^{2+} > Ca^{2+} > Mg^{2+}$ and for aluminium it is highest. This sequence refers to the fact that there are very few cations in the membrane phase, and so in both the cases, the current carrying species are the cations. The change on the ion has a very big effect on the mobility of the ions in the membranes. As the charge on the counter ions is increased, the membrane resistance increases. This may be ascribed to be due to the

Table 1
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $10 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C ₁) (M) $\times 10^4$	E _{obs} (mV)	E+C (mV)	E _m (mV)	R _m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	49.10	75.00	-55.60	666.60	0.68
1.0	11.50	49.10	74.00	-55.00	666.60	0.70
1.5	12.00	48.60	72.90	-54.40	659.00	0.85
2.0	12.50	48.10	71.60	-53.80	640.00	0.90
2.5	14.00	47.20	70.20	-51.90	610.00	0.93
3.0	15.00	46.50	69.00	-50.90	568.00	0.97
3.5	18.00	46.00	68.00	-48.00	525.00	1.05
4.0	20.00	46.00	67.00	-44.00	500.00	1.10

Vide Figs. 2,3,4.

Table 2
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $15 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C ₁) (M) $\times 10^4$	E _{obs} (mV)	E+C (mV)	E _m (mV)	R _m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	45.50	96.50	-60.10	571.40	3.60
1.0	12.00	45.00	95.20	-59.80	563.40	3.50
1.5	13.50	44.60	94.00	-56.80	535.70	3.70
2.0	14.00	44.40	92.80	-55.60	520.00	3.90
2.5	16.00	44.10	91.20	-52.90	520.00	4.40
3.0	18.00	44.00	89.50	-50.00	476.00	4.90
3.5	19.00	43.70	88.50	-49.70	442.30	5.00
4.0	20.00	43.50	87.50	-48.80	440.00	5.20

Vide Figs. 2, 3 and 4

Table 3
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C ₁) (M) $\times 10^4$	E _{obs} (mV)	E ⁺ _C (mV)	E _m (mV)	R _m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.50	42.00	98.80	-67.60	377.70	4.10
1.0	11.00	41.80	97.50	-66.60	356.00	4.30
1.5	12.00	41.50	96.00	-65.20	355.00	4.40
2.0	13.00	41.00	95.50	-64.00	333.00	5.20
2.5	14.50	40.70	94.70	-61.40	329.50	5.40
3.0	15.00	40.30	93.30	-59.70	307.00	5.70
3.5	17.00	40.10	91.80	-58.90	287.00	6.00
4.0	19.00	40.00	90.50	-56.80	284.00	6.00

Vide Figs. 2, 3 and 4

Table 4
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C ₁) (M) $\times 10^4$	E _{obs} (mV)	E ⁺ _C (mV)	E _m (mV)	R _m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.00	40.10	99.50	-68.60	283.40	4.31
1.0	12.50	40.00	98.00	-67.70	268.00	4.80
1.5	13.00	39.70	96.20	-66.70	260.00	4.70
2.0	14.00	39.30	95.00	-64.70	241.00	4.96
2.5	15.00	39.00	94.00	-64.30	243.00	4.98
3.0	17.00	38.70	93.50	-61.00	225.60	6.01
3.5	18.50	38.65	92.20	-58.05	219.00	6.80
4.0	20.00	38.50	91.00	-55.90	215.00	6.81

Vide Figs. 2, 3 and 4

Table 5
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $10 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C ₁) (M) $\times 10^4$	E _{obs} (mV)	E _{+C} (mV)	E _m (mV)	R _m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.00	19.50	86.00	-83.00	850.00	0.37
1.0	13.50	19.00	84.80	-81.20	812.50	0.45
1.5	14.00	18.70	83.40	-80.40	787.50	0.58
2.0	16.00	18.40	82.00	-77.60	783.70	0.63
2.5	18.00	18.00	80.70	-76.00	723.60	0.67
3.0	18.50	17.70	79.30	-74.70	702.70	0.76
3.5	19.50	17.50	78.00	-73.80	648.60	0.85
4.0	21.00	17.40	77.00	-71.60	645.00	0.87

Vide Figs. 5m 6 and 7

Table 6
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $15 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C ₁) (M) $\times 10^4$	E _{obs} (mV)	E _{+C} (mV)	E _m (mV)	R _m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.00	17.30	90.00	-87.50	766.60	0.80
1.0	12.50	17.20	89.00	-86.50	711.00	0.82
1.5	13.50	17.00	88.00	-85.00	700.00	1.10
2.0	15.00	16.70	87.00	-82.50	647.70	1.10
2.5	16.50	16.50	86.00	-80.40	628.00	1.20
3.0	18.00	16.10	84.80	-78.50	600.00	1.40
3.5	19.00	15.70	83.50	-77.70	577.60	1.50
4.0	20.00	15.50	82.30	-76.80	535.00	1.70

Vide Figs. 5m 6 and 7

Table 7
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	15.10	98.00	-93.90	856.20	1.30
1.0	12.00	15.00	96.50	-91.10	561.40	1.40
1.5	13.00	14.50	95.20	-89.00	534.40	1.50
2.0	14.00	14.10	93.90	-88.50	500.00	1.70
2.5	15.00	14.00	92.30	-86.90	500.00	1.80
3.0	17.00	13.80	91.00	-84.60	463.60	1.90
3.5	18.00	13.50	90.00	-83.30	454.00	2.00
4.0	19.00	13.20	89.00	-81.90	418.10	2.20

Vide Figs. 5, 6 and 7

Table 8
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $25 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	11.70	101.50	-98.50	540.00	1.40
1.0	12.00	11.30	100.20	-96.50	540.00	1.50
1.5	14.00	11.10	99.00	-93.30	500.00	1.60
2.0	15.00	11.00	97.80	-91.60	463.00	1.80
2.5	17.00	10.40	96.30	-88.80	444.40	2.00
3.0	20.00	10.20	95.20	-85.30	420.00	2.20
3.5	20.50	10.00	94.00	-84.40	400.00	2.30
4.0	21.00	9.80	93.00	-84.00	370.00	2.50

Vide Figs. 5, 6 and 7

Table 9

Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through Cobalt Phosphate Membrane at $10 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	15.90	90.00	-89.90	891.00	0.11
1.0	11.80	15.40	89.00	-88.80	881.00	0.21
1.5	13.50	15.00	88.00	-86.30	850.00	0.21
2.0	15.00	14.50	87.00	-84.10	821.00	0.37
2.5	18.00	14.00	86.00	-80.00	784.00	0.56
3.0	19.00	13.60	84.80	-79.30	780.00	0.70
3.5	20.00	13.20	83.50	-78.60	779.00	0.71
4.0	21.00	13.00	82.30	-77.10	770.00	0.75

Vide Figs. 8, 9 and 10

Table 10

Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through Cobalt Phosphate Membrane at $15 \pm 0.1^{\circ}\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.00	13.30	100.00	-96.80	840.00	0.39
1.0	13.00	13.00	98.00	-90.70	833.00	0.43
1.5	15.00	12.50	96.20	-87.80	773.30	0.59
2.0	16.00	12.10	95.00	-86.50	766.60	0.85
2.5	16.50	11.70	94.00	-86.30	760.00	0.91
3.0	18.00	11.40	93.00	-84.30	750.00	1.10
3.5	20.00	11.00	92.20	-82.50	755.00	1.20
4.0	22.00	10.50	91.00	-80.10	750.00	1.30

Vide Figs. 8, 9 and 10

Table 11
Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs} (mV)	E _{+C} (mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/ S)
0.5	12.00	10.50	105.00	-99.10	755.50	0.46
1.0	13.00	10.10	103.80	-92.00	742.20	0.57
1.5	14.00	9.80	102.30	-90.00	733.30	0.89
2.0	15.00	9.70	101.00	-87.70	697.60	1.10
2.5	16.50	9.40	99.70	-87.40	951.10	1.10
3.0	17.50	9.00	98.00	-87.30	616.20	1.40
3.5	19.00	8.70	96.50	-87.00	581.00	1.50
4.0	20.00	8.50	95.00	-85.50	570.00	2.10

Vide Figs. 8, 9 and 10

Table 12
Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs} (mV)	E _{+C} (mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/ S)
0.5	13.50	7.70	110.00	-101.00	666.60	0.58
1.0	15.00	7.50	109.00	-99.30	647.00	0.64
1.5	16.50	7.10	108.00	-98.50	610.00	1.00
2.0	18.00	6.70	107.20	-97.10	570.00	1.30
2.5	18.50	6.00	106.00	-95.50	531.00	1.70
3.0	19.00	5.60	104.70	-94.10	520.00	2.20
3.5	19.50	5.50	103.20	-92.40	510.00	2.30
4.0	21.00	5.20	102.00	-91.60	510.00	2.50

Vide Figs. 8, 9 and 10

Table 13
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	4.80	91.50	-88.70	615.30	0.47
1.0	13.00	4.50	90.50	-86.20	610.00	0.57
1.5	14.50	4.10	89.50	-84.40	581.80	0.68
2.0	16.50	3.80	88.50	-81.30	596.70	0.75
2.5	18.00	3.40	87.50	-80.00	565.50	0.88
3.0	19.50	2.90	86.30	-78.80	564.40	0.90
3.5	22.00	2.50	85.00	-76.40	557.00	1.00
4.0	23.00	2.10	83.80	-76.30	550.00	1.00

Vide 11, 12 and 13

Table 14
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.00	0.00	101.50	-94.00	517.20	0.72
1.0	14.50	-0.50	99.50	-90.60	512.70	0.85
1.5	17.00	-0.90	97.70	-87.00	500.00	0.86
2.0	18.00	-1.50	96.50	-86.40	465.00	0.91
2.5	19.00	-1.80	95.50	-85.70	458.80	0.92
3.0	20.00	-2.20	94.50	-84.80	463.00	0.92
3.5	22.00	-2.70	93.70	-83.10	457.00	1.10
4.0	23.00	-3.00	92.50	-82.80	462.00	1.20

Vide Figs. 11, 12 and 13

Table 15
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + \text{C}$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.00	-3.50	106.50	-99.20	400.00	0.81
1.0	12.50	-4.00	105.30	-99.10	386.00	0.91
1.5	14.00	-4.50	103.80	-97.30	375.00	0.95
2.0	16.00	-4.90	102.50	-94.20	362.00	1.20
2.5	18.00	-5.30	101.20	-91.70	345.50	1.30
3.0	19.50	-5.80	99.50	-90.40	342.30	1.30
3.5	20.00	-6.00	98.50	-90.10	350.00	1.30
4.0	20.00	-6.20	98.50	-90.00	350.00	1.30

Vide Figs. 11, 12 and 13

Table 16
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + \text{C}$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.00	-5.10	111.50	-102.50	284.80	1.40
1.0	13.00	-5.50	110.50	-101.70	275.00	1.60
1.5	14.00	-6.00	109.50	-100.40	272.10	1.60
2.0	16.00	-6.50	108.70	-97.40	260.00	2.00
2.5	17.50	-7.00	107.50	-95.50	254.00	2.30
3.0	19.00	-7.50	106.20	-94.20	245.10	2.70
3.5	20.00	-8.00	104.70	-93.40	241.00	3.10
4.0	21.00	-8.30	103.50	-92.70	240.00	3.20

Vide Figs. 11, 12 and 13

Table 17
Values of Parameters For The Diffusion of BaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.50	1.50	94.50	-93.10	430.00	0.17
1.0	11.50	1.10	93.30	-91.30	425.00	0.19
1.5	13.50	0.70	92.50	-87.80	425.00	0.49
2.0	14.50	0.10	91.50	-87.30	432.00	0.50
2.5	16.00	-0.80	90.50	-86.30	423.40	0.51
3.0	18.00	-1.50	89.30	-83.80	422.60	0.63
3.5	19.50	-1.80	88.00	-82.40	416.60	0.67
4.0	21.00	-2.00	86.80	-80.90	416.00	0.83

Vide Fig. 14, 15 and 16

Table 18
Values of Parameters For The Diffusion of BaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	-2.70	103.00	-97.30	340.00	0.69
1.0	11.50	-3.00	102.00	-97.00	333.30	0.76
1.5	13.00	-3.70	100.20	-95.50	340.00	0.76
2.0	15.00	-4.00	99.00	-92.40	332.00	0.93
2.5	15.50	-4.70	98.00	-91.90	331.00	0.98
3.0	17.00	-5.20	97.00	-90.70	330.00	1.00
3.5	19.00	-5.80	95.20	-88.40	327.00	1.10
4.0	20.00	-6.00	94.00	-87.50	327.00	1.20

Vide Fig. 14, 15 and 16

Table 19
Values of Parameters For The Diffusion of BaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	-6.00	109.40	-102.30	290.60	1.10
1.0	12.00	-6.50	108.40	-101.00	287.60	1.10
1.5	12.50	-6.80	106.50	-100.70	290.00	1.20
2.0	13.50	-7.00	105.50	-99.20	289.00	1.30
2.5	15.00	-7.50	104.00	-97.40	288.00	1.40
3.0	16.00	-7.90	102.40	-96.10	288.00	1.40
3.5	17.50	-8.10	101.00	-95.30	287.00	1.60
4.0	18.00	-8.50	99.50	-94.30	205.00	1.80

Vide Figs. 14, 15 and 16

Table 20
Values of Parameters For The Diffusion of BaCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.50	-9.10	114.50	-108.80	275.00	1.20
1.0	11.00	-9.70	113.50	-107.60	267.00	1.30
1.5	11.50	-10.00	112.50	-107.00	275.00	1.40
2.0	12.50	-11.60	111.70	-106.30	265.60	1.40
2.5	14.00	-11.00	110.50	-104.20	267.00	1.50
3.0	16.00	-11.50	109.20	-101.20	269.00	1.60
3.5	17.00	-12.00	107.70	-100.50	264.70	1.80
4.0	19.00	-12.80	106.50	-98.40	260.70	1.90

Vide Figs. 14, 15 and 16

Table 21
Values of Parameters For The Diffusion of MgCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + c$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.50	10.45	55.10	-59.50	460.00	0.58
1.0	13.00	10.10	53.60	-57.10	430.00	0.71
1.5	15.00	9.75	52.00	-54.00	428.00	0.87
2.0	16.50	9.20	50.80	-52.30	350.00	0.99
2.5	17.50	8.70	49.40	-49.00	276.00	1.40
3.0	19.50	8.35	47.90	-48.30	271.00	1.50
3.5	20.50	8.10	46.40	-47.80	271.00	1.50
4.0	21.50	8.00	45.00	-47.40	260.70	1.60

Vide Figs. 17, 18 and 19

Table 22
Values of Parameters For The Diffusion of MgCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + c$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	7.55	60.10	-62.40	367.20	0.96
1.0	12.50	7.15	58.60	-61.80	350.00	1.00
1.5	13.50	6.50	57.00	-59.80	346.70	1.30
2.0	16.50	6.00	55.80	-56.70	336.70	1.40
2.5	18.00	5.50	54.40	-54.80	310.30	1.60
3.0	19.00	4.70	52.90	-52.00	258.00	1.80
3.5	19.00	4.10	51.40	-51.30	254.50	1.80
4.0	20.00	4.00	50.00	-51.30	239.50	1.90

Vide Figs. 17, 18 and 19

Table 23
Values of Parameters For The Diffusion of MgCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.50	5.75	64.30	-66.00	310.80	1.30
1.0	14.00	5.50	62.80	-63.50	300.00	1.50
1.5	15.50	5.20	61.30	-62.10	290.00	1.50
2.0	17.00	5.00	59.80	-58.20	277.70	1.60
2.5	19.00	4.50	58.40	-56.40	211.20	1.70
3.0	20.00	4.10	56.90	-55.60	200.00	2.20
3.5	21.00	3.80	55.40	-54.70	170.00	2.20
4.0	21.00	3.70	54.00	-54.60	170.00	2.50

Vide Figs. 17, 18 and 19

Table 24
Values of Parameters For The Diffusion of MgCl_2 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	3.00	68.30	-71.30	266.60	1.40
1.0	12.50	2.75	66.80	-68.60	244.40	1.60
1.5	13.50	2.45	65.30	-67.10	240.00	1.70
2.0	15.00	2.10	63.80	-65.20	238.40	1.80
2.5	16.50	1.80	62.40	-63.10	200.00	2.20
3.0	17.50	1.30	60.90	-62.40	190.00	2.30
3.5	18.00	1.00	58.40	-61.10	180.00	3.20
4.0	19.00	0.50	58.00	-61.40	153.00	3.30

Vide Figs. 17, 18 and 19

Table 25
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.50	-18.20	85.00	-100.00	500.00	0.60
1.0	11.50	-19.60	83.80	-99.70	500.00	1.00
1.5	13.50	-21.80	82.40	-98.00	495.00	1.20
2.0	14.50	-21.50	81.40	-96.00	490.00	1.50
2.5	16.00	-22.30	81.00	-94.50	488.00	2.00
3.0	18.00	-22.00	79.70	-92.00	480.00	2.30
3.5	19.50	-21.60	77.00	-91.00	476.20	2.70
4.0	21.00	-22.40	76.00	-89.00	470.00	2.80

Vide Figs. 20, 21 and 22

Table 26
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	-19.20	89.00	-102.50	460.00	1.30
1.0	11.50	-19.50	88.00	-101.00	459.00	1.90
1.5	13.00	-21.30	87.00	-100.00	458.00	2.10
2.0	15.00	-22.30	86.00	-97.50	451.00	2.50
2.5	15.50	-20.30	85.00	-95.00	450.00	2.50
3.0	17.00	-19.60	83.80	-92.50	440.50	3.20
3.5	19.00	-20.00	82.50	-91.00	435.40	3.10
4.0	20.00	-21.00	81.30	-90.00	432.00	4.90

Vide Figs. 20, 21 and 22

Table 27
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	-21.40	97.00	-106.10	440.00	4.00
1.0	12.00	-22.20	95.50	-104.00	435.80	4.40
1.5	12.50	-21.60	94.20	-102.20	434.50	4.80
2.0	13.50	-22.10	92.90	-101.00	431.50	5.30
2.5	15.00	-23.00	91.30	-99.50	412.20	5.50
3.0	16.00	-23.00	90.00	-98.00	409.00	6.00
3.5	17.50	-23.90	89.00	-97.00	405.20	6.50
4.0	18.00	-24.00	88.00	-96.50	390.00	6.80

Vide Figs. 20, 21 and 22

Table 28
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Phosphate Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E + C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.50	-27.10	100.50	-113.20	400.00	5.40
1.0	11.00	-27.50	99.20	-111.50	391.70	5.50
1.5	11.50	-25.50	98.00	-108.50	390.00	5.80
2.0	12.50	-23.40	96.80	-106.00	377.40	6.60
2.5	14.00	-26.00	95.30	-104.50	360.00	6.50
3.0	16.00	-27.30	94.20	-103.00	358.00	7.60
3.5	17.00	-30.60	93.00	-101.50	342.00	9.00
4.0	19.00	-30.80	92.00	-100.00	300.00	9.50

Vide Figs. 20, 21 and 22

Table 29

Values of Parameters For The Diffusion of monovalent, divalent and trivalent electrolytes at The end of 1/2 and 4 hour periods Through Cobalt Phosphate Membrane at $25 \pm 0.1^{\circ}\text{C}$

Parameters Electrolyte	E_{obs} (mV)	E_{+C} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/s)					
	$\frac{1}{2}\text{h} \leftrightarrow 4\text{ h}$									
KCl	40.10	38.50	99.50	-68.60	283.40	215.0	4.30	6.80		
NaCl	11.70	9.80	101.50	93.00	-98.50	-84.00	540.00	370.0	1.40	2.70
LiCl	7.70	5.20	110.00	102.00	-101.40	-91.60	666.60	500.0	0.60	2.50
CaCl ₂	-5.10	-8.30	111.50	103.50	-102.50	-92.70	284.80	240.0	1.40	3.20
BaCl ₂	-9.10	-12.80	114.50	106.50	-108.80	-98.40	275.00	260.7	1.20	1.90
NgCl ₂	3.00	0.50	68.30	58.00	-71.30	-61.40	266.60	153.0	1.40	3.30
AlCl ₃	-27.10	-30.80	100.50	92.00	-113.20	-100.00	400.00	300.0	0.50	0.90

Table 30

Values of Parameters For The Diffusion of monovalent, divalent and trivalent electrolytes at The end of 1/2 and 4 hour periods Through nickel Phosphate Membrane at $25 \pm 0.1^{\circ}\text{C}$

Parameters Electrolyte	E_{obs} (mV)	E_{+C} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/s)					
	$\frac{1}{2}\text{h} \leftrightarrow 4\text{ h}$									
KCl	44.10	42.00	98.00	91.00	-64.40	-51.40	261.50	110.0	6.40	11.10
NaCl	15.70	13.00	99.50	97.00	-94.50	-80.20	426.00	285.2	1.30	4.10
LiCl	10.50	8.30	108.00	100.00	-98.00	-88.00	475.50	342.2	2.10	4.00
CaCl ₂	-4.00	-7.00	110.00	103.00	-101.30	-91.40	265.00	205.2	1.60	2.90
BaCl ₂	-6.50	-8.30	111.50	103.50	-106.20	-94.40	260.00	235.0	1.00	1.90
NgCl ₂	5.70	3.50	66.20	55.00	-68.00	-58.40	218.00	140.0	2.10	4.00
AlCl ₃	-24.10	-25.00	99.00	90.50	-110.20	-97.00	382.20	340.8	0.60	0.80

Vide Figs. 23-25

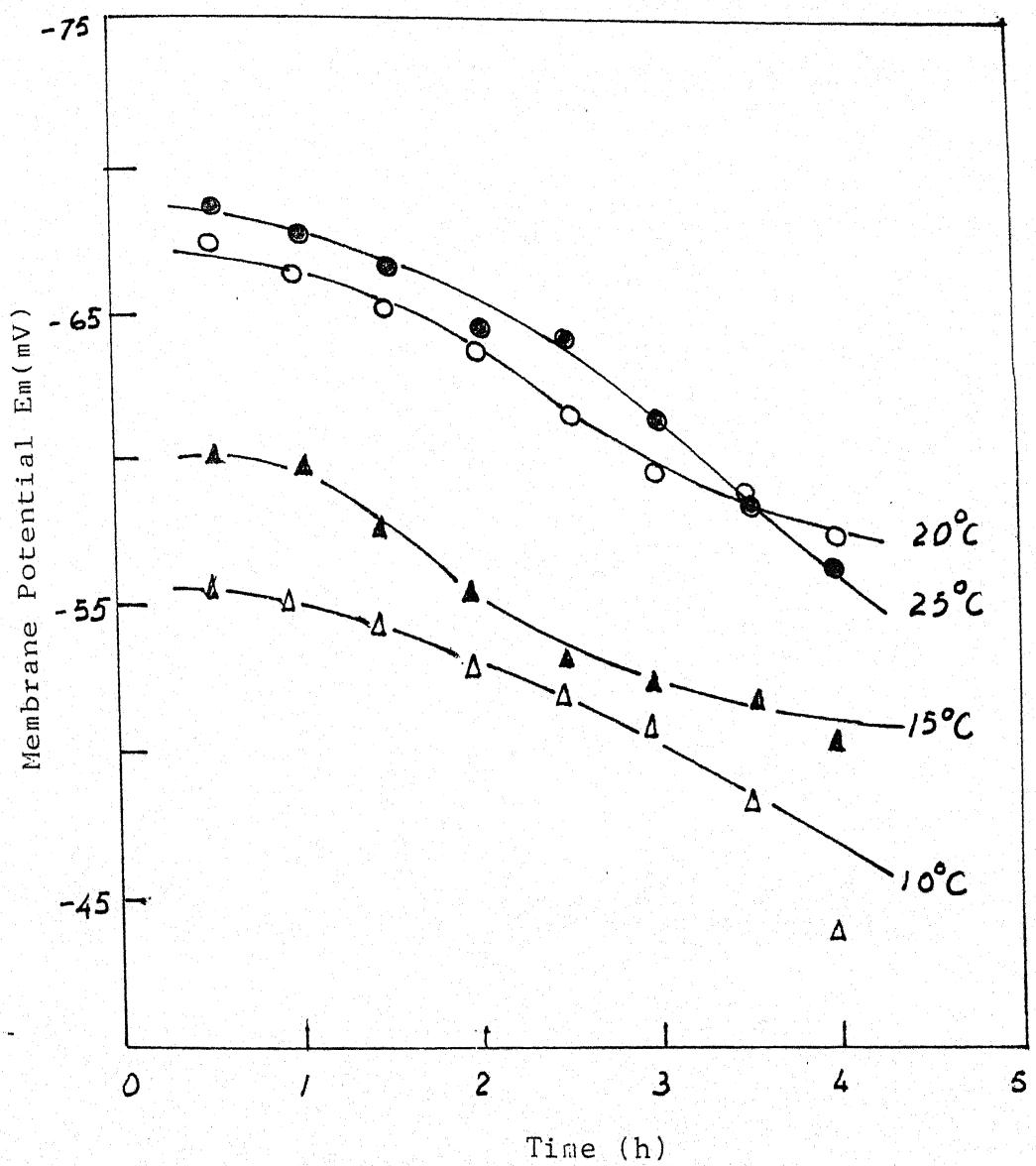


FIG.2. Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt phosphate membrane using KCl electrolyte.

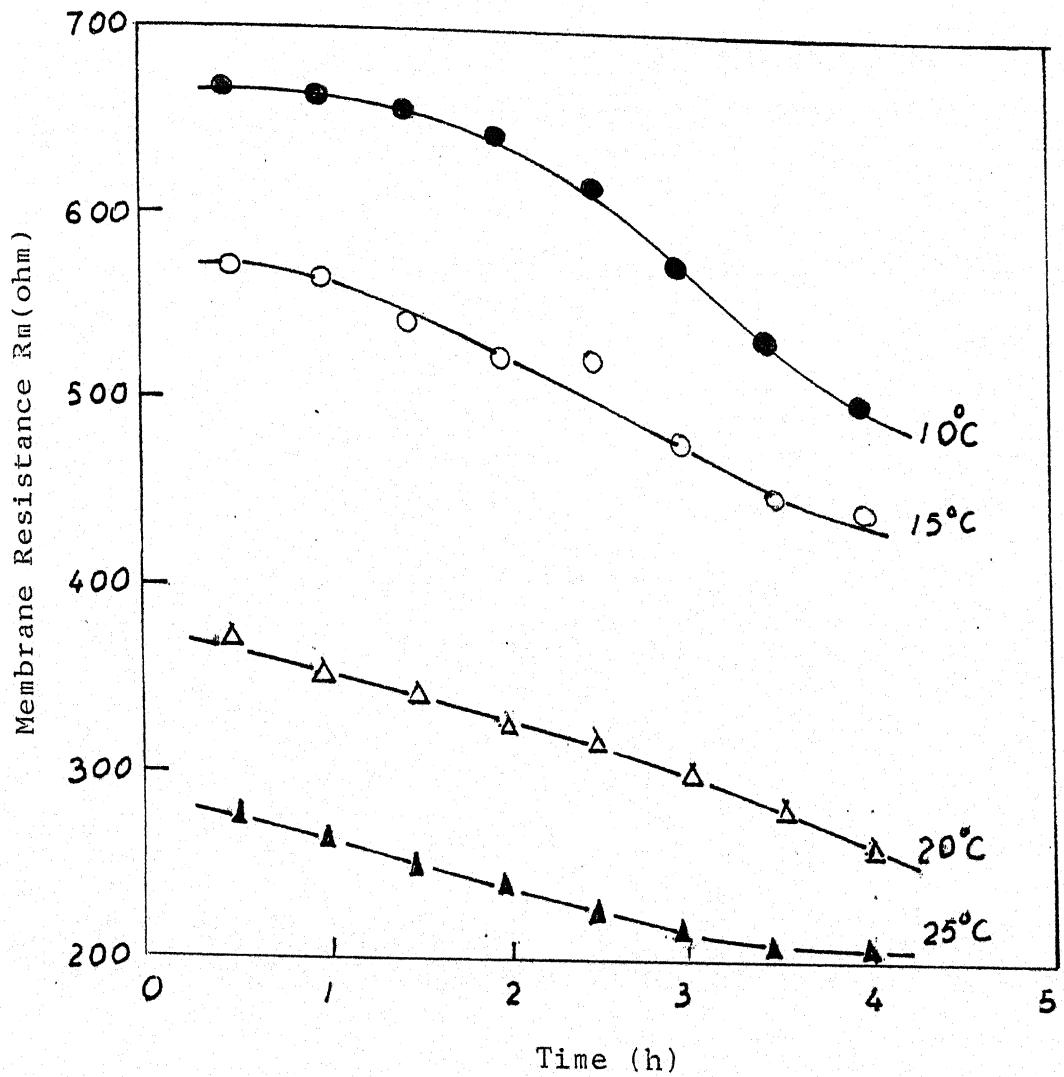


FIG.3. Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt phosphate membrane using KCl electrolyte.

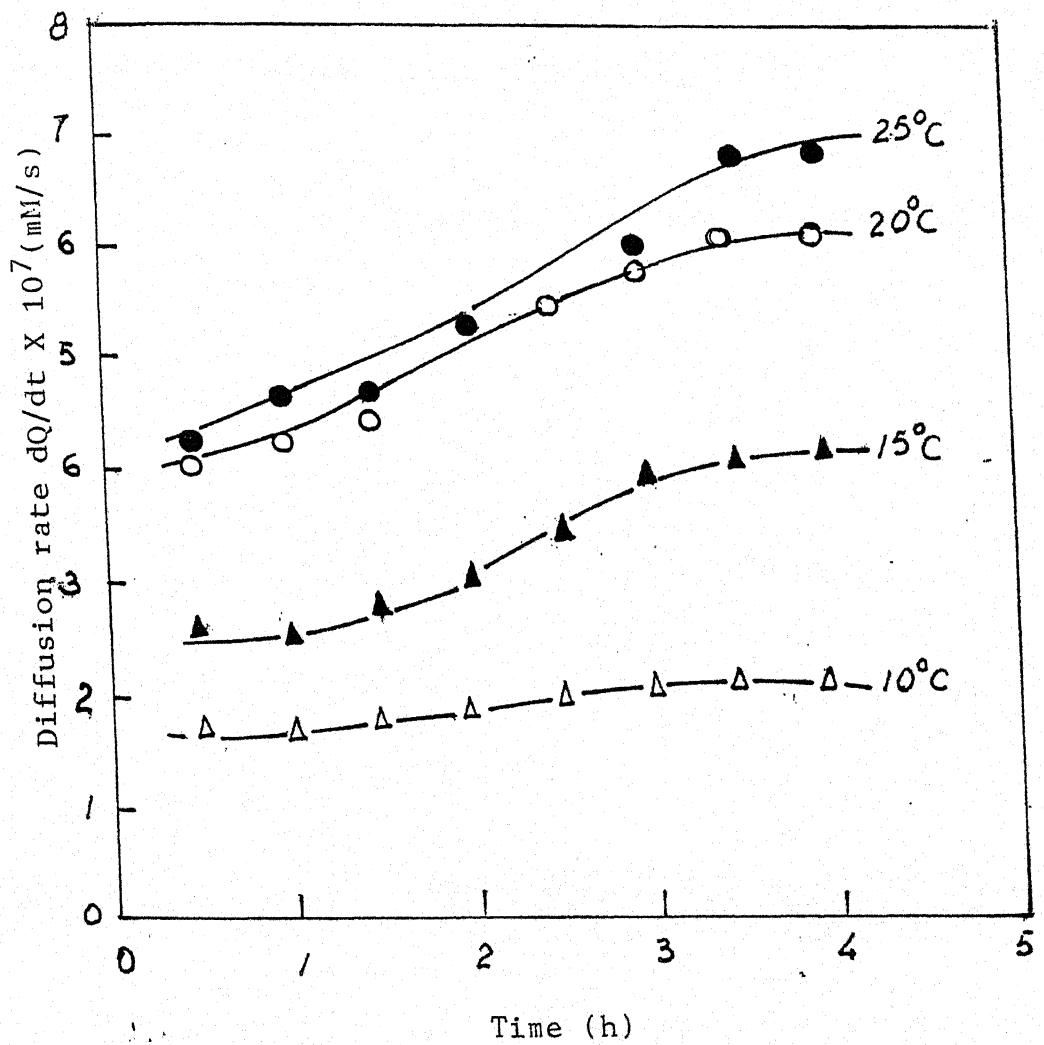


FIG.4. Plots of diffusion rate dQ/dt (mM/s) against time (h) at different temperatures across cobalt phosphate membrane using KCl electrolyte.

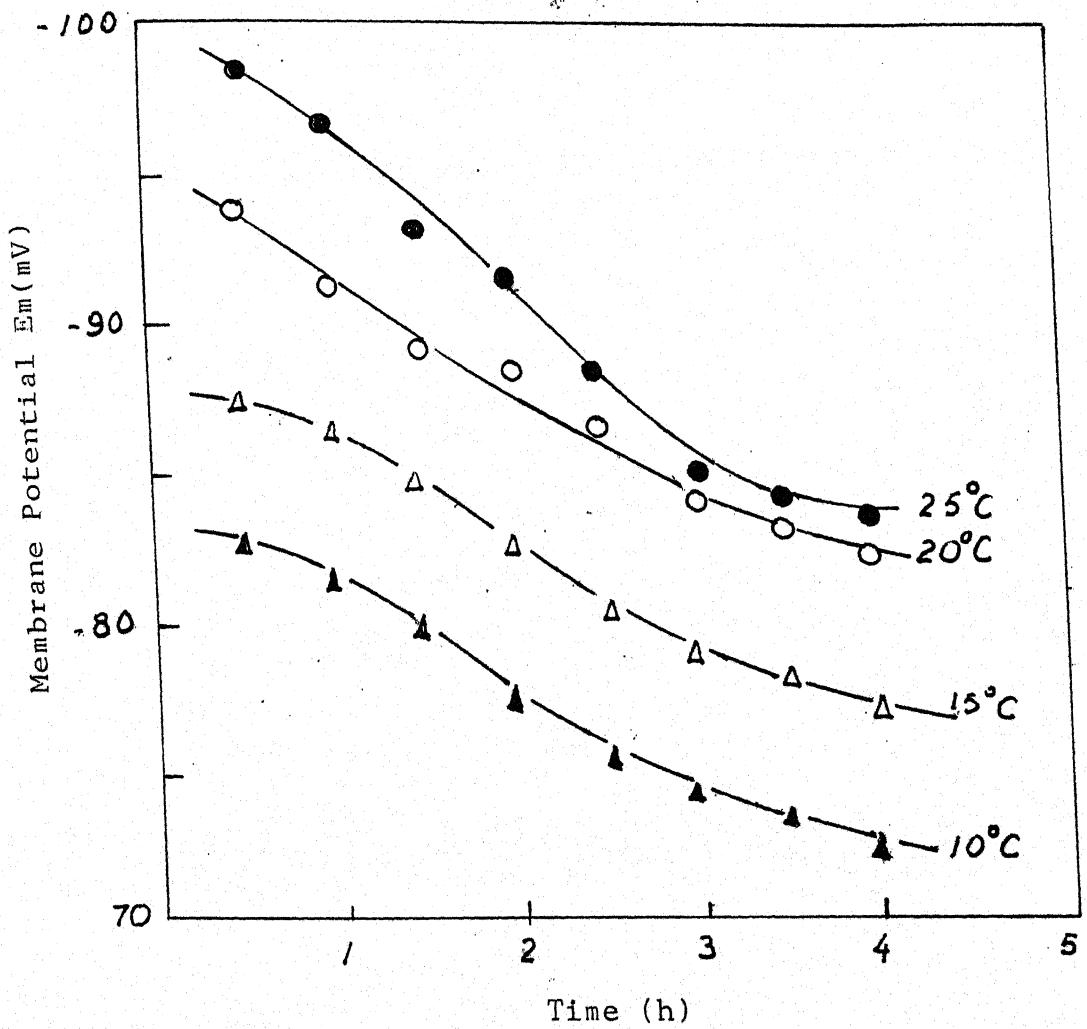


FIG.5. Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt phosphate membrane using NaCl electrolyte.

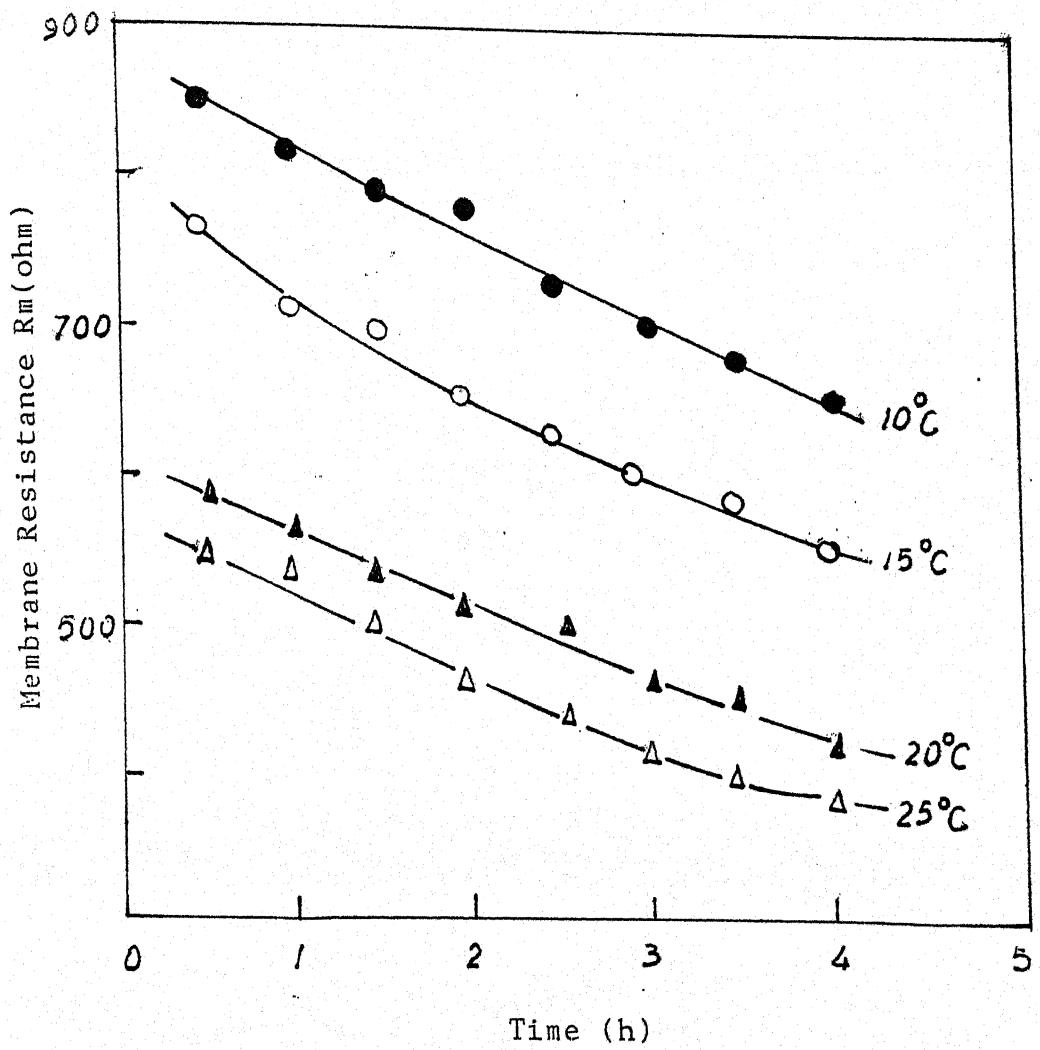


FIG.6. Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt phosphate membrane using NaCl electrolyte.

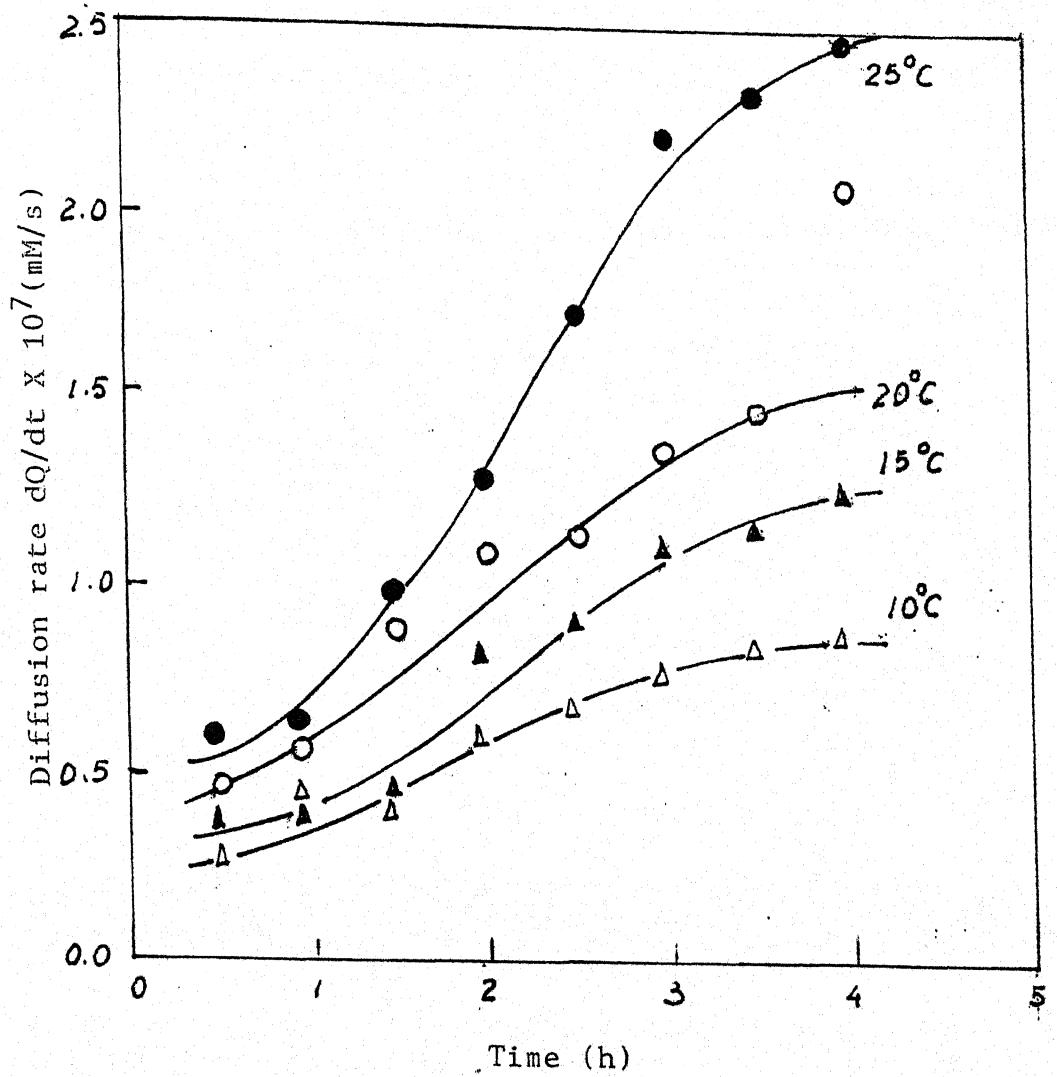


FIG.7. Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across cobalt phosphate membrane using NaCl electrolyte.

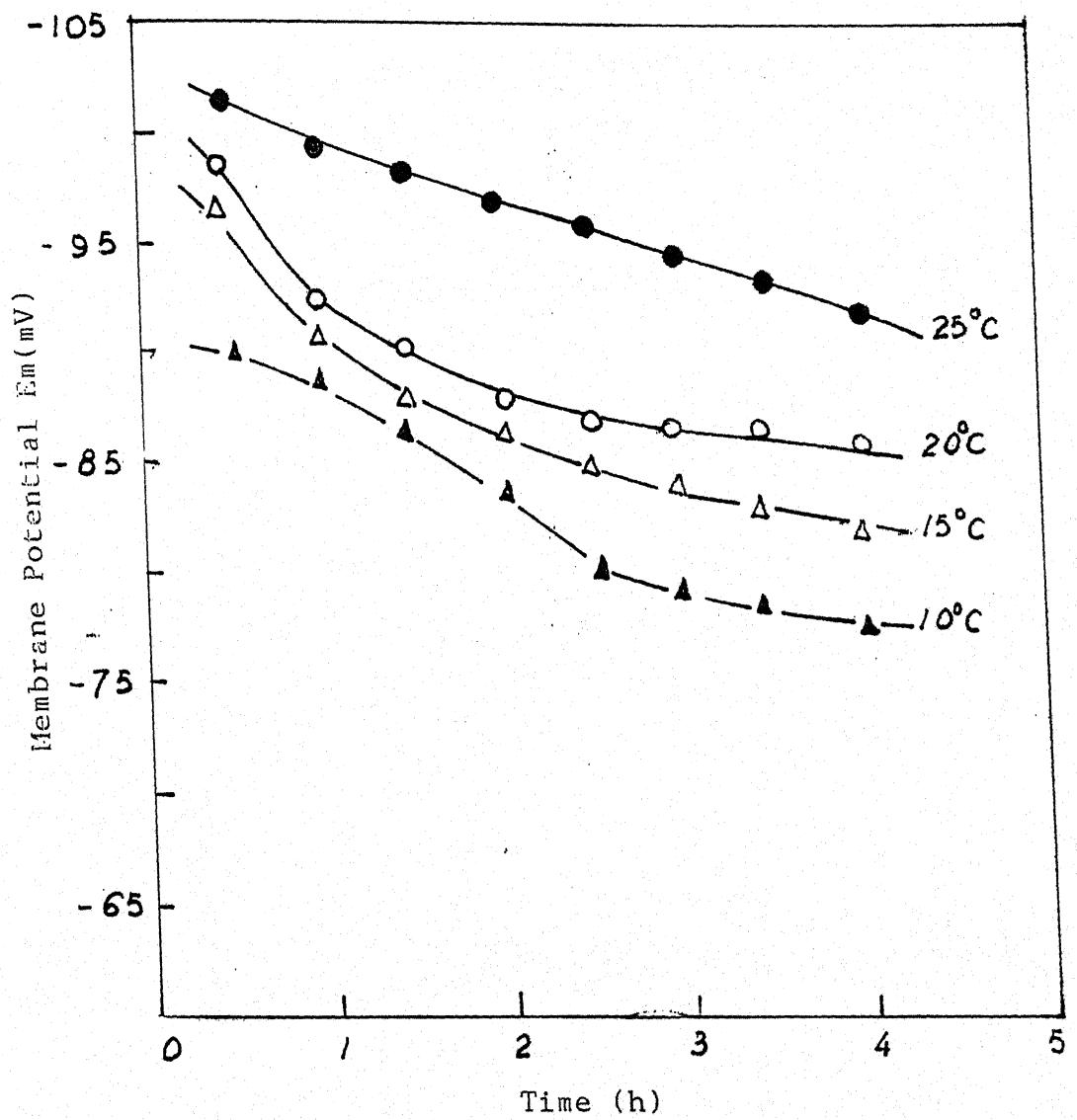


FIG.8. Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt phosphate membrane using LiCl electrolyte.

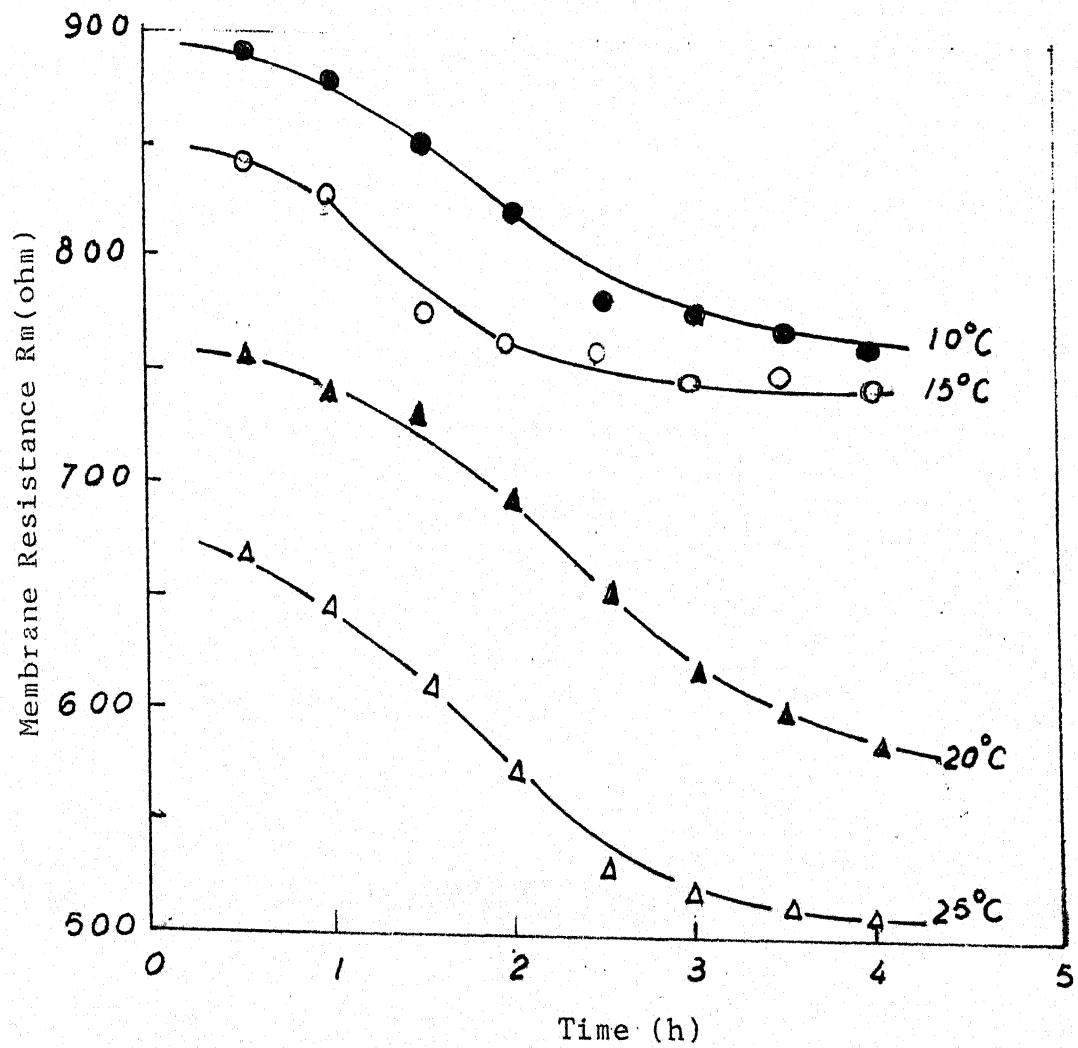


FIG.9. Plots of membrane resistance R_m (Ohm) against Time (h) at different temperatures across cobalt phosphate membrane using LiCl electrolyte.

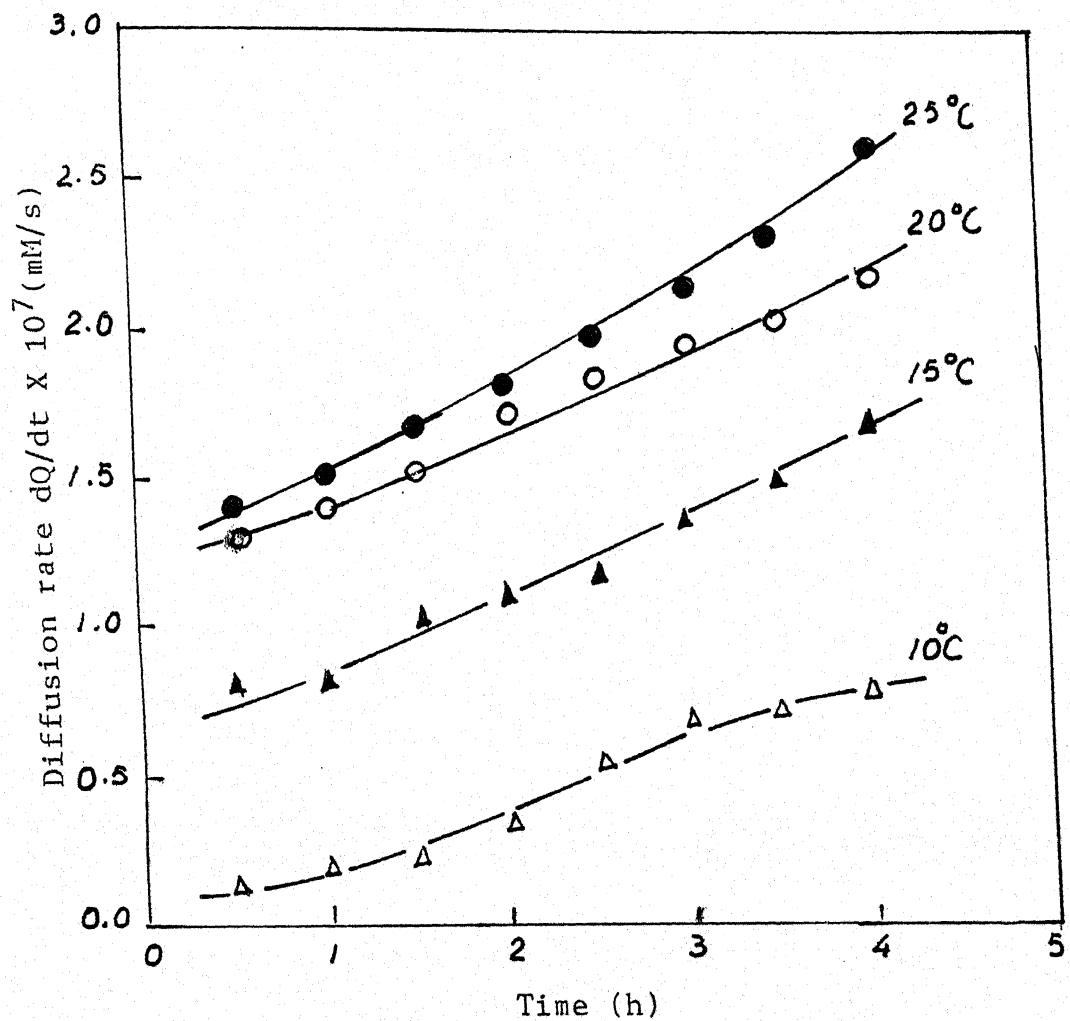


FIG.10. Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across cobalt phosphate membrane using LiCl electrolyte.

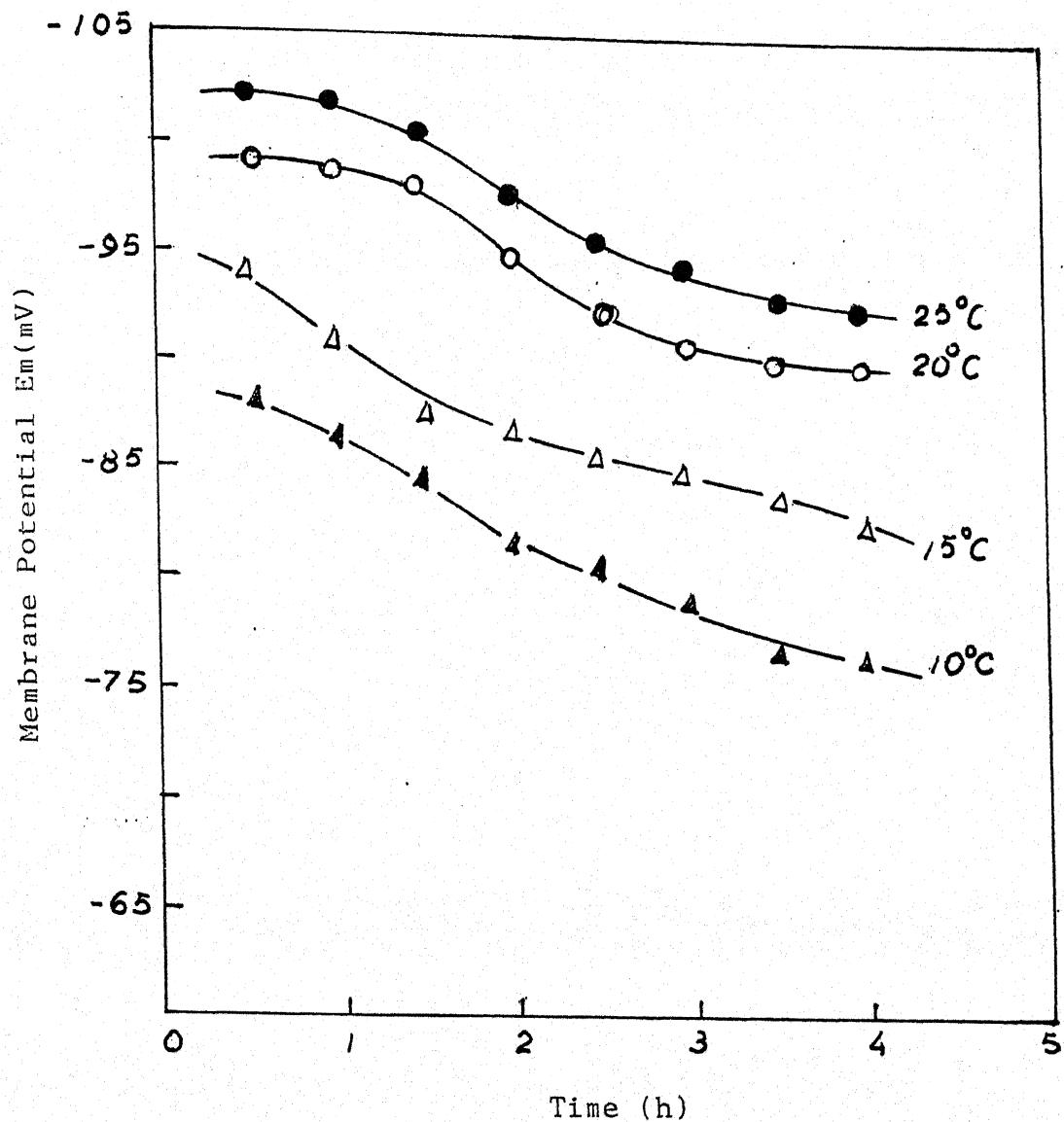


FIG.11. Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt phosphate membrane using CaCl_2 electrolyte.

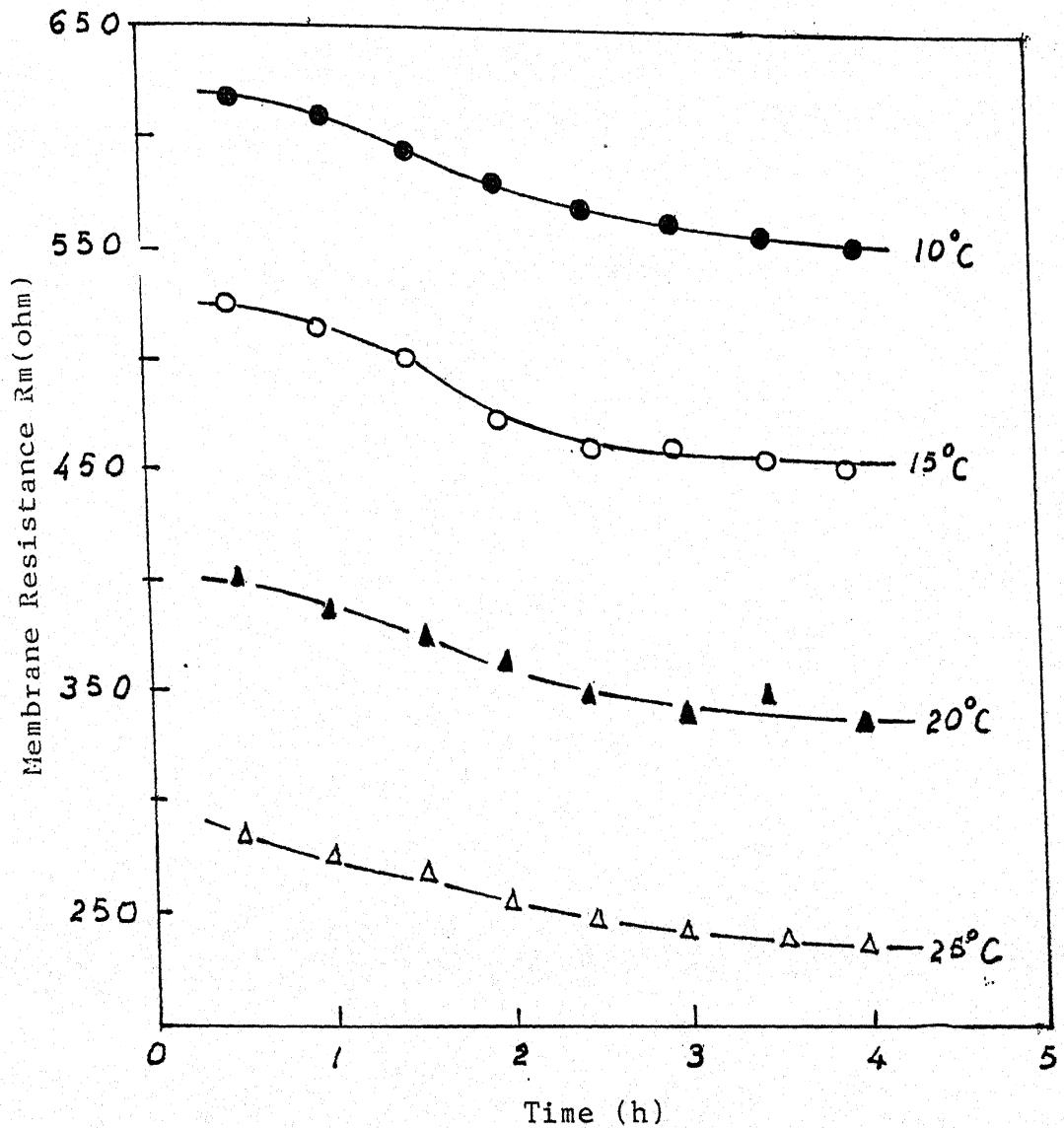


FIG.12. Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt phosphate membrane using CaCl_2 Electrolyte.

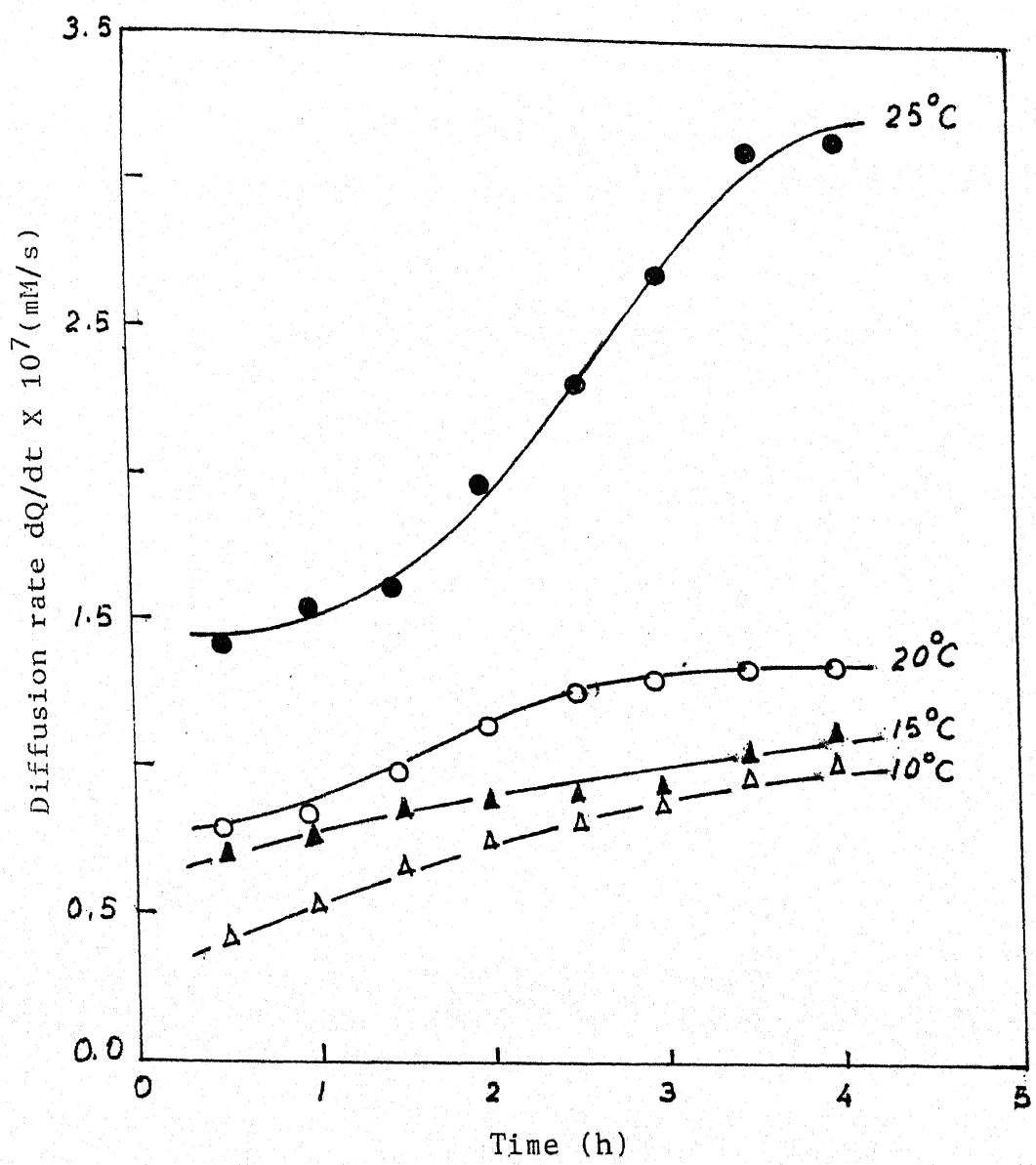


FIG.13. Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across cobalt phosphate membrane using CaCl_2 electrolyte.

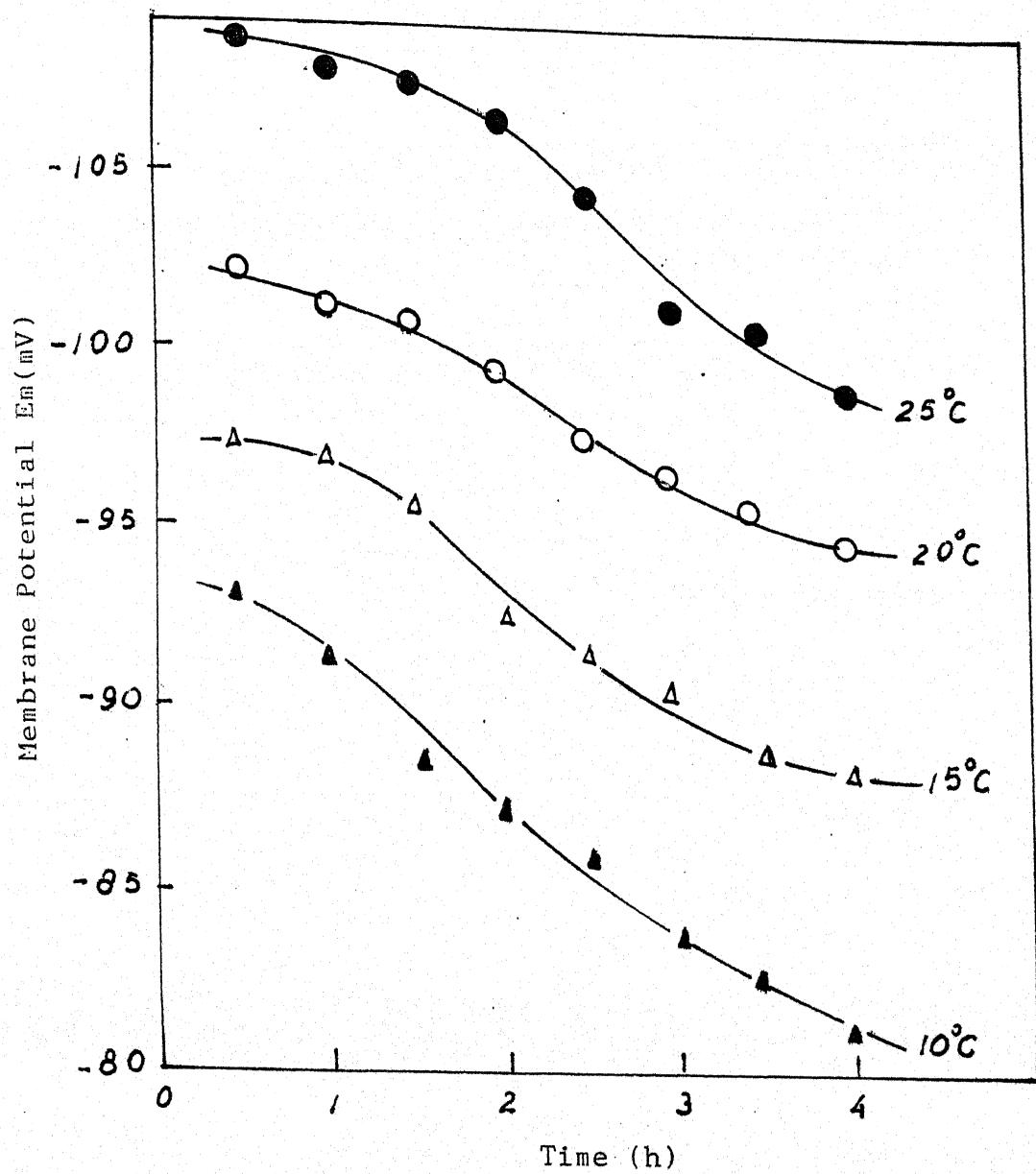


FIG.14. Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt phosphate membrane using BaCl_2 electrolyte.

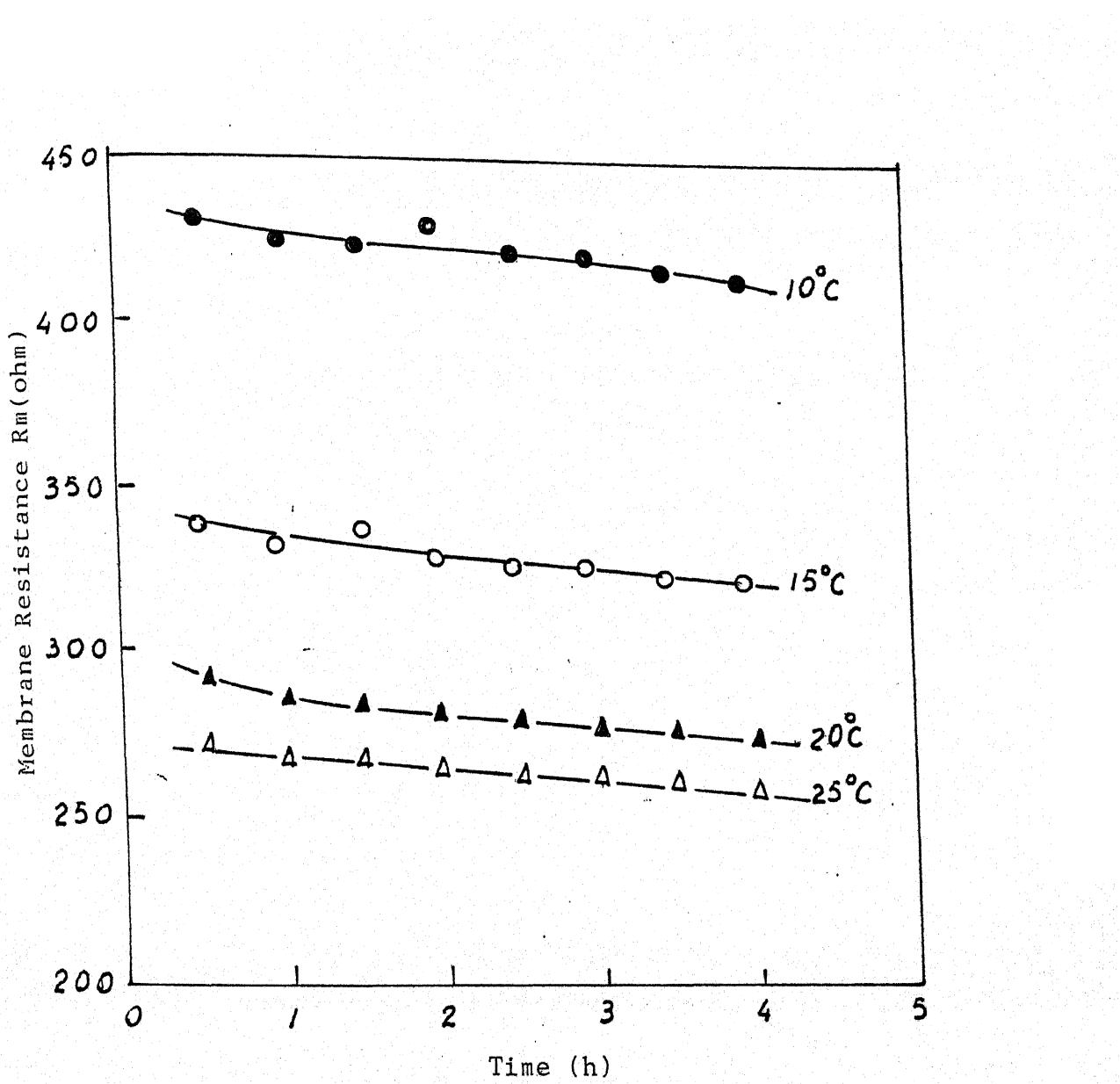


FIG.15. Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt phosphate membrane using BaCl_2 electrolyte.

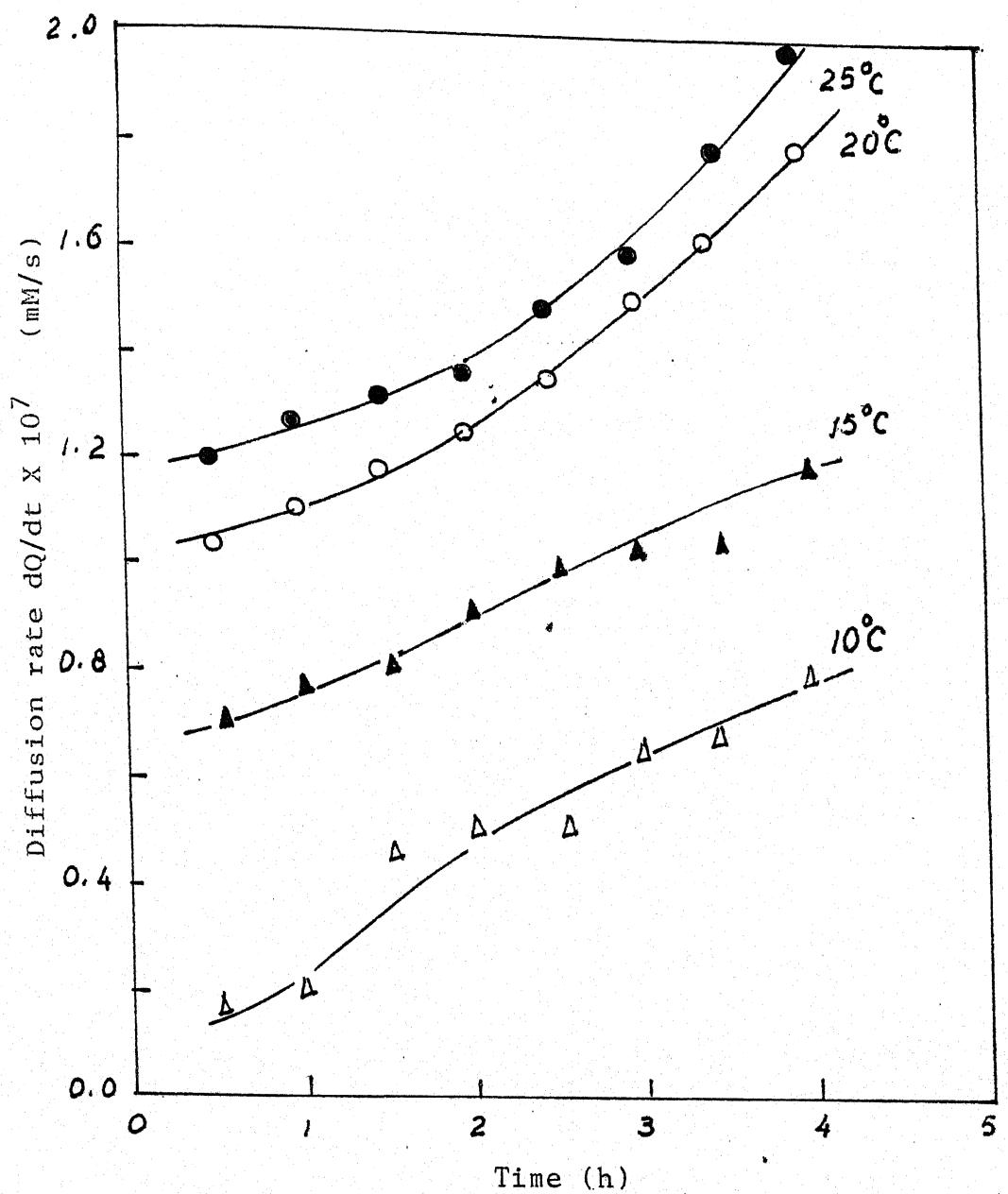


FIG.16. Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperature across cobalt phosphate membrane using BaCl_2 electrolyte.

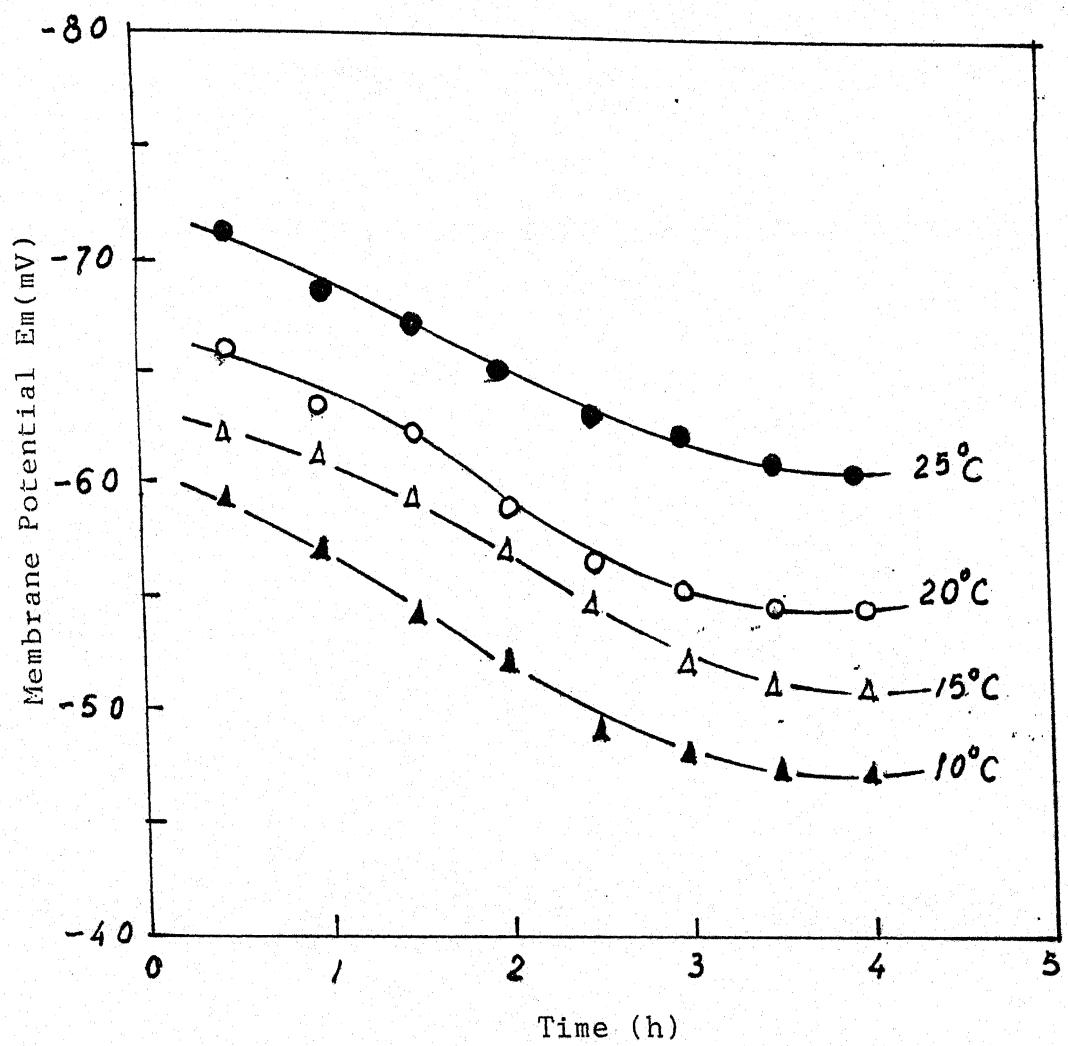


FIG.17. Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt phosphate membrane using $MgCl_2$ electrolyte.

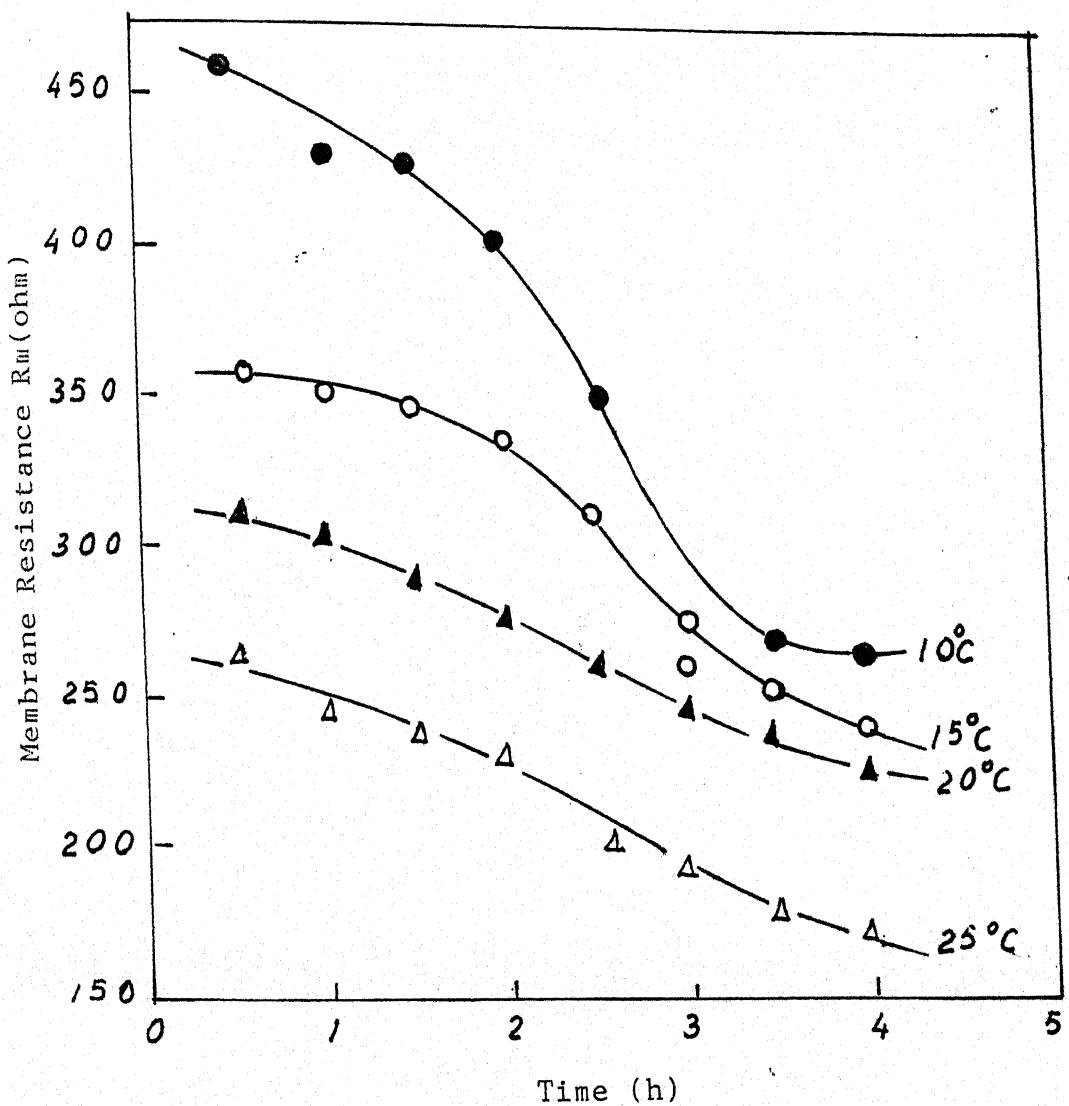


FIG.18. Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt phosphate membrane using $MgCl_2$ electrolyte.

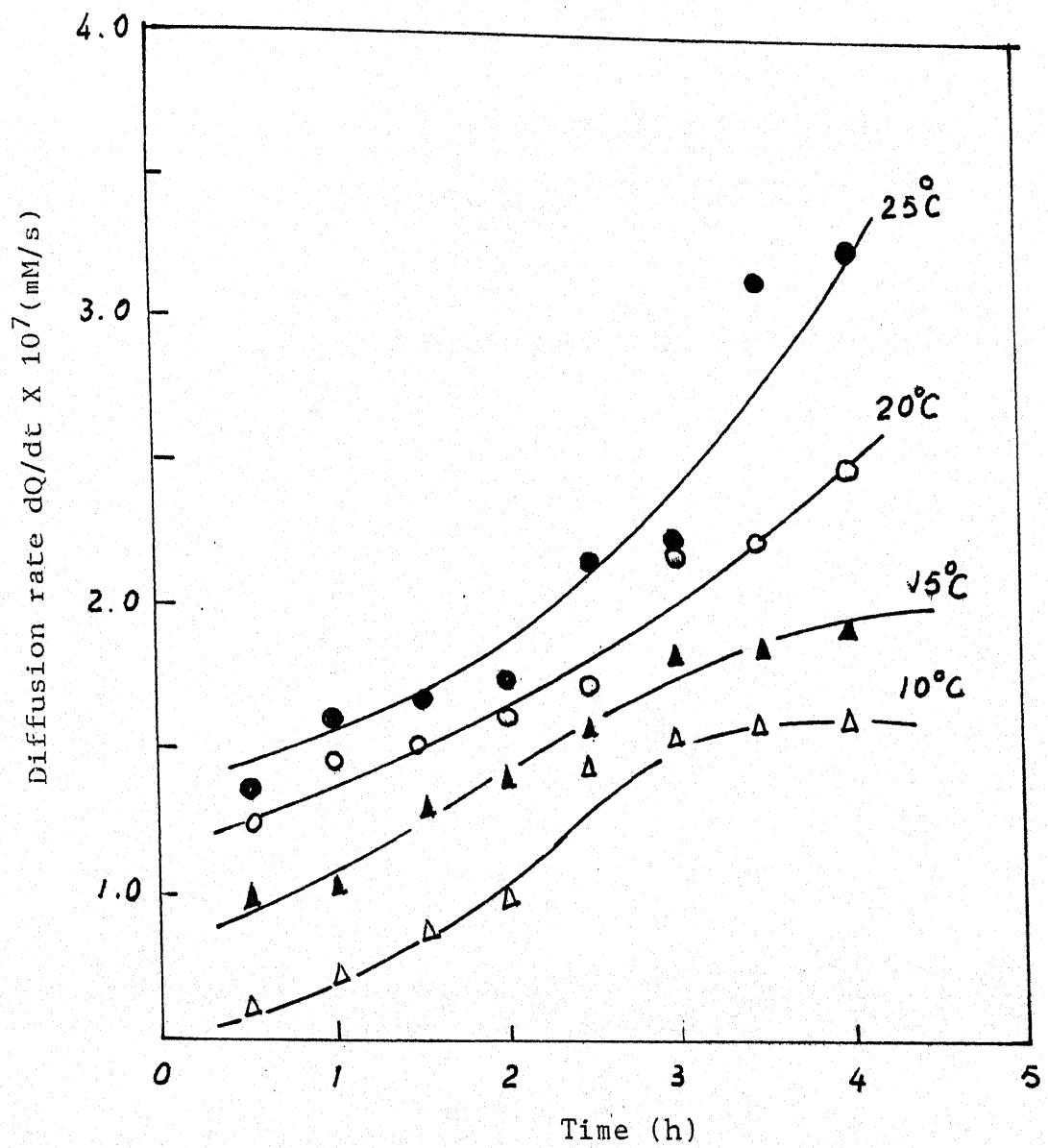


FIG.19. Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across cobalt phosphate membrane using $MgCl_2$ electrolyte.

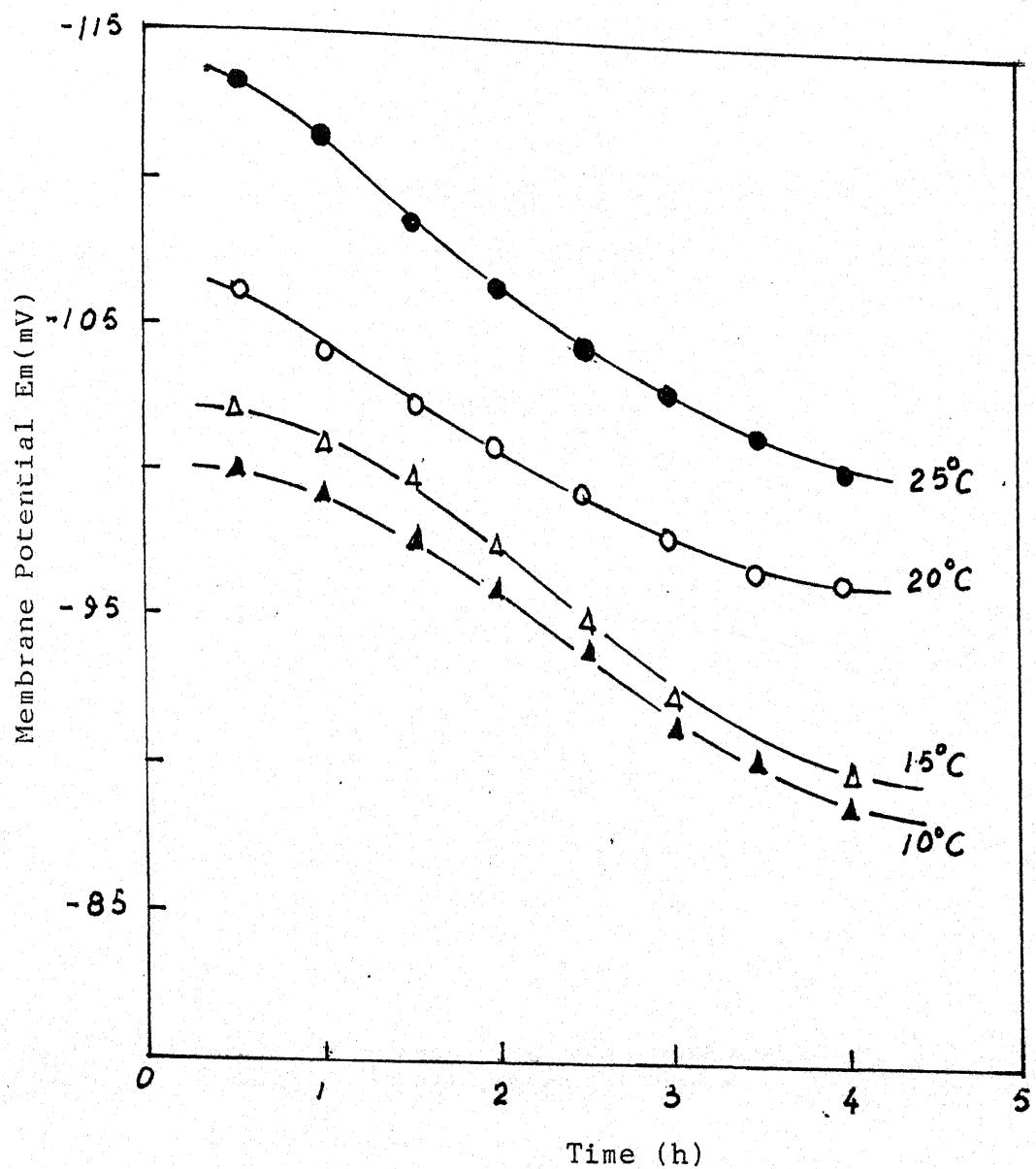


FIG.20. Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt phosphate membrane using AlCl_3 electrolyte.

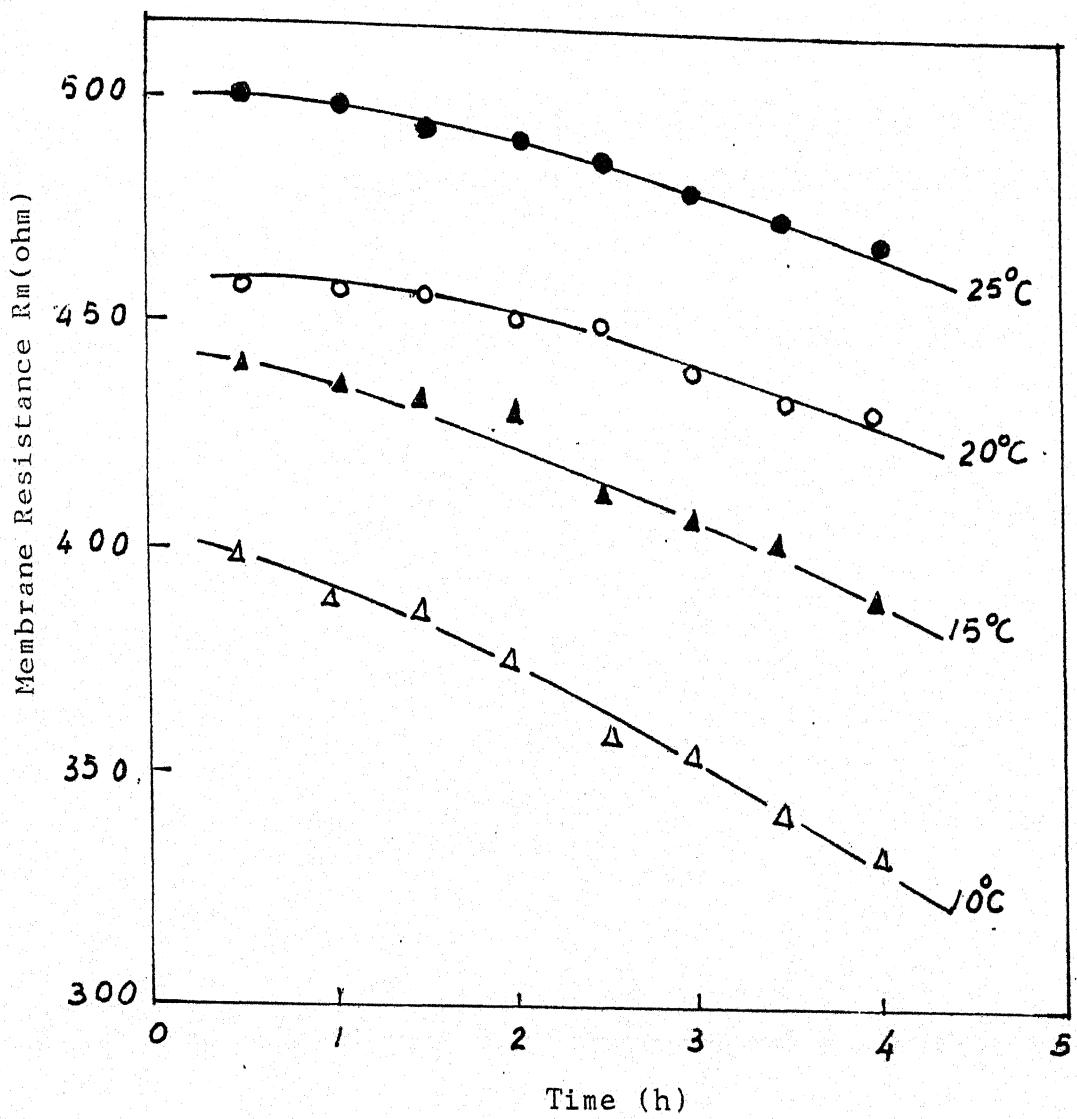


FIG.21. Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt phosphate membrane using $AlCl_3$ electrolyte.

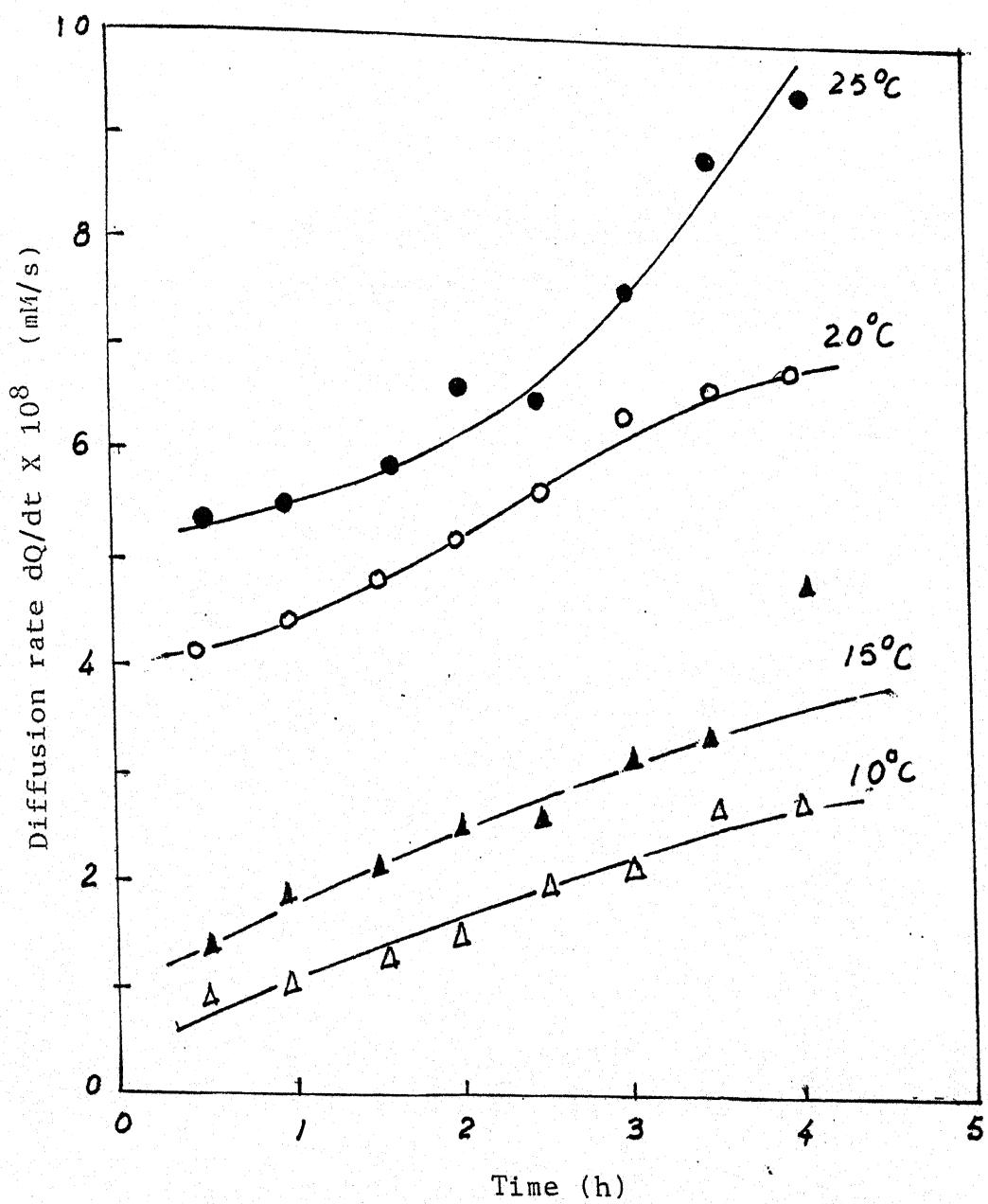


FIG.22. Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across cobalt phosphate membrane using AlCl_3 electrolyte.

Membrane Potential E_m (mV)

-100
-80
-60
-40
-20

I AlCl_3
II BaCl_2
III CaCl_2
IV LiCl
V NaCl
VI MgCl_2
VII KCl

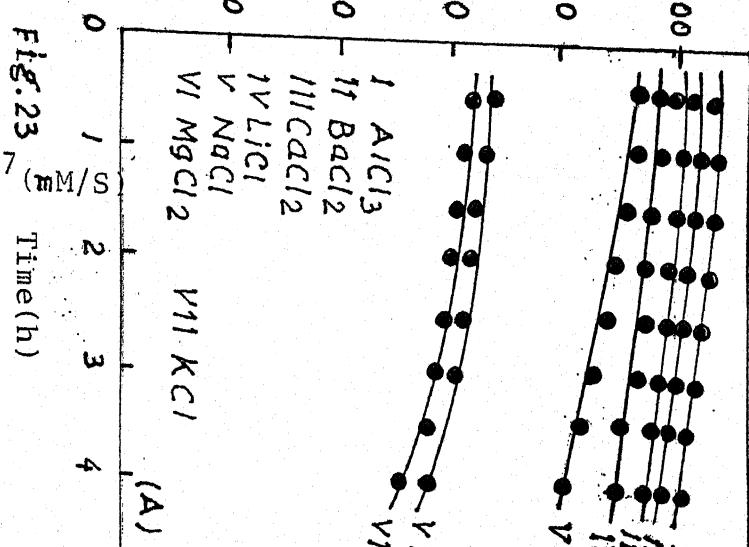


Fig. 24

Time(h)

Membrane Resistance R_m (ohm)

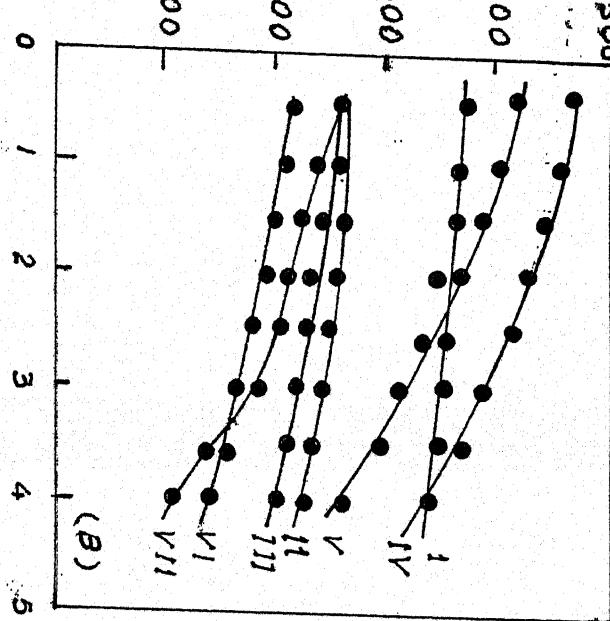


Fig. 23

Time(h)

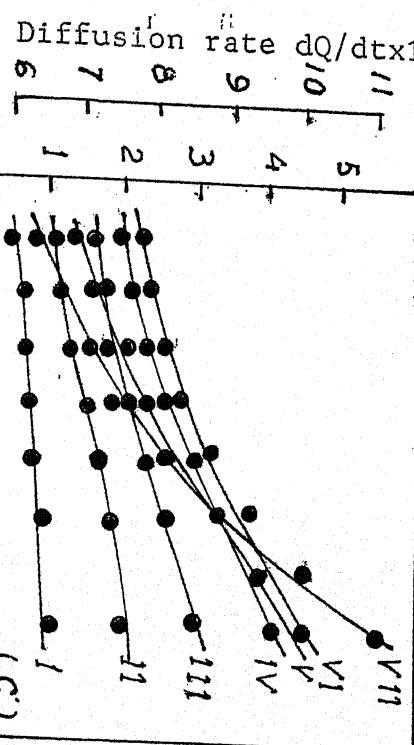


Fig. 25

Time(h)

Plots of (A) Membrane potential E_m (mV) (B) Membrane Resistance R_m (ohm) (C) Diffusion Rate $dQ/dt \times 10^7$ (mM/S) against time (h) Across Nickel Phosphate Membrane at 25°C

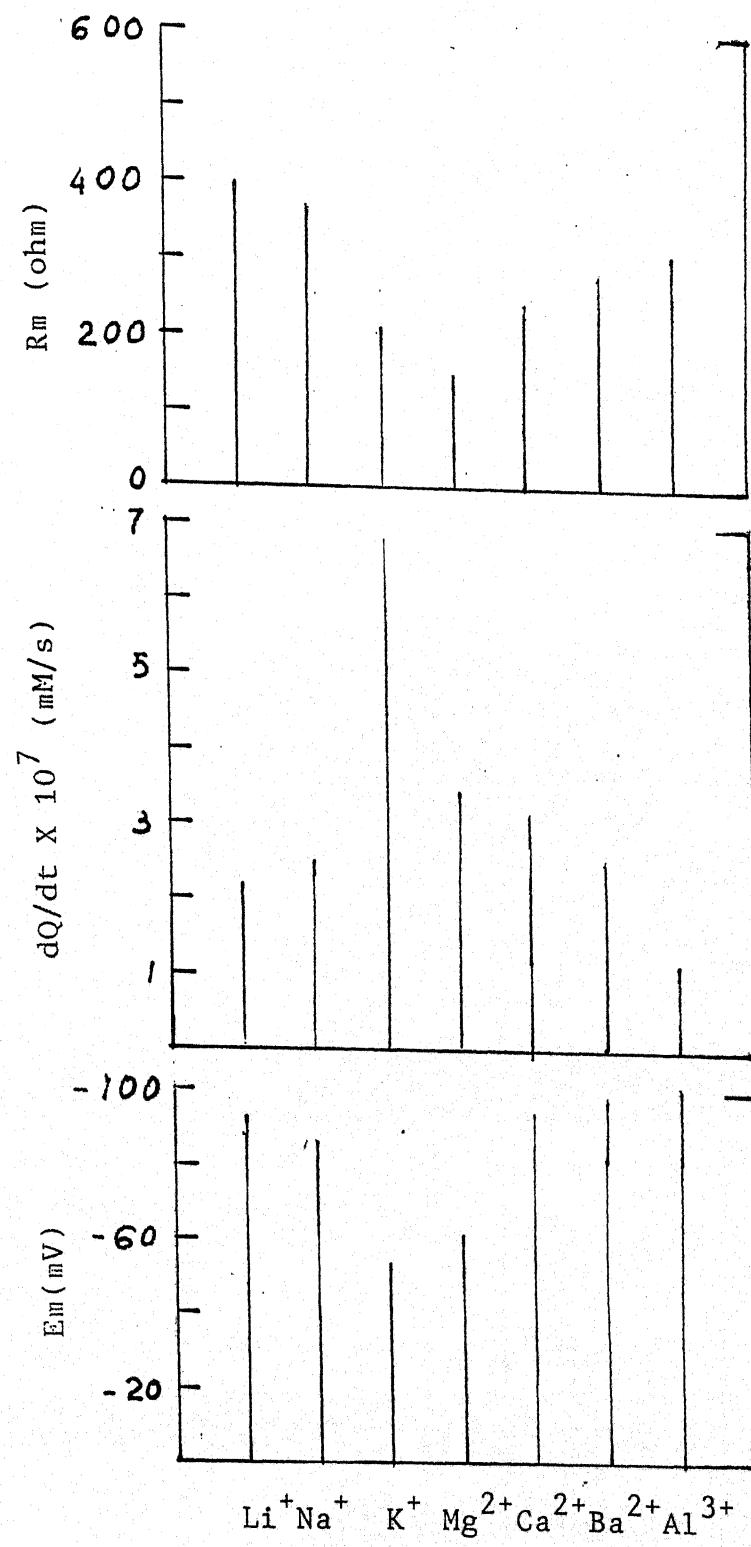


FIG.26. Plots of E_m , R_m , and dQ/dt against various electrolytes across cobalt phosphate membrane at $25^\circ C$.

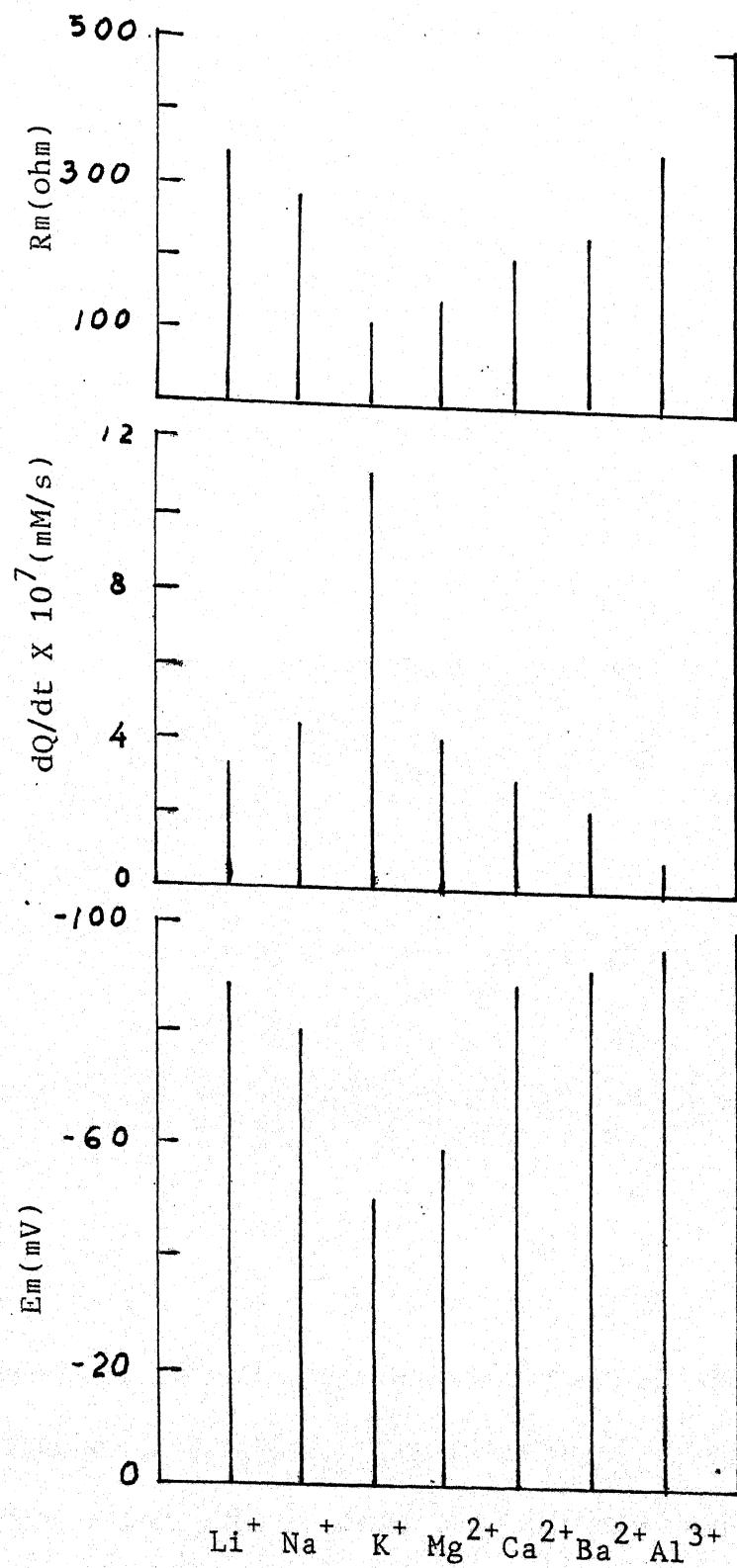


FIG.27. Plots of E_m , R_m , and dQ/dt against various electrolytes across nickel phosphate membrane at 25°C .

increase in the ion association with the membrane exchange groups. This is in agreement with the findings of Subrahmanyam and Lakshminarayanaiah (49) and Gregor and co-workers (50) for the AMF C- 103 membrane and our own findings with parchment supported inorganic precipitate membranes (30,33,35).

The values of Em decreases with time though almost to a negligible extent, as can be seen, in Fig. 23 for various diffusing electrolytes through parchment supported nickel phosphate membrane. The slight change in Em may be due to the small changes produced in the concentration of electrolyte solutions during the diffusion process. The membrane potential sequence for alkali metal ions was $Li^+ > Na^+ > K^+$ and for multivalent cations it was $Al^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+}$. This sequence of membrane potential points towards the fact that multivalent ions are more strongly adsorbed on the membrane skeleton than univalent ions and that aluminium being most strongly adsorbed (30).

The values of diffusion rate dQ/dt for various cations were calculated from the predetermined values of membrane potential Em and membrane resistance Rm using eqs. (4-6). The diffusion of electrolytes through the membrane is slower than in free solution. This may be due to various reasons: (a) only a part of framework is available for free diffusion, (b) the diffusion paths in the membrane phase are more tortuous and therefore longer, (c) the larger hydrated ions in the narrow mesh region of the membrane be 'impeded in their mobility by the framework and (d) the interaction of the diffusing species with the fixed groups on the membrane matrix. The diffusion rate sequence of cations diffusing through the

membrane was $K^+ > Na^+ > Li^+ >$ and $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$. This diffusion rate sequence on the basis of Eisenman-Sherry model of membrane selectivity (41,43,51) point towards weak field strength of charge groups attached to the membrane matrix. This is in agreement with our earlier findings of inorganic precipitate membranes (23-31).

Parchment paper, except for the presence of some stray and end carboxyl groups, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on the membrane surface in the case of dilute solutions of electrolyte (1: 1) leading to the type of ionic distribution associated with the electrical double layer. However, use of concentrated electrolyte (1: 1) or (2: 1) or (3: 1) leaves a net positive charge on the membrane surface due to preferential adsorption of cations. This type of charge reversal is not peculiar to these systems. Rosenberg et al. (52) found in the case of thorium counterions, negative electroosmotic transport of water. The ion was so thoroughly adsorbed on a cation exchange membrane that it conferred anion selectivity to the membrane and thus water was transferred in the opposite direction. Similarly Schulz, (53) found, in the case of sodium diphosphate, adsorption of the diphosphate anion on the surface of the anion exchange membranes permplex A-100. This reversed the charge on the membrane and also the direction of water flow.

The system under consideration may be taken as having charged capillary structures or gels which can be judged in the light of classical fixed charge theory of Teorlls (54); Meyer and Sievers (55); Sollner (56); He et al. (57) Paloty and Hoch et al. (58,59). Flow of electrolyte by diffusion because of the presence of a net charge (-ve or +ve) on the membrane gives

rise to the membrane potential as opposed to the liquid junction potential ordinarily under similar conditions in the absence of the membrane, which regulates the flow of electrolyte by increasing the speed of slow moving ion and by decreasing the speed of the faster moving ion. The regulated rate of flow for various electrolytes through the investigated membranes follow the sequence $K^+ > Na^+ > Li^+$ and $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$.

Membrane porosity in the relation to the size of the species (hydrated) flowing through the membrane seems to determine the above sequence. Although the sizes of the hydrated electrolytes are not known with certainty, because of few tabulations (60-61) of the number of moles of water associated with some electrolytes. However, in Fig. 28 a plot of permeability of different electrolytes (chlorides) against free energy of hydration of cations (62) is given for both the membranes. It is seen that permeability decreases with increasing hydration energy, that is, greater size due to "increase in hydration. This points to the fact that the electrolyte is diffusing along the 'pores or channels of dimensions adequate enough to allow the substance to penetrate the membrane. The state of hydration of penetrating electrolyte may be considered to exist in a dynamic condition so that at higher temperatures considerably higher fraction 'F' of the total number of a given kind would posses excess energy, ΔE according to the Boltzman distribution $f = e^{-\Delta E/RT}$ (R is the gas content). Under these circumstances, those ionic species which have lost sufficient water of hydration to be smaller than the size of the pore would enter the membrane. In this way, the permeability would increase with increase in temperature, subject, however, to the privo so that the membrane has undergone no irreversible change in its

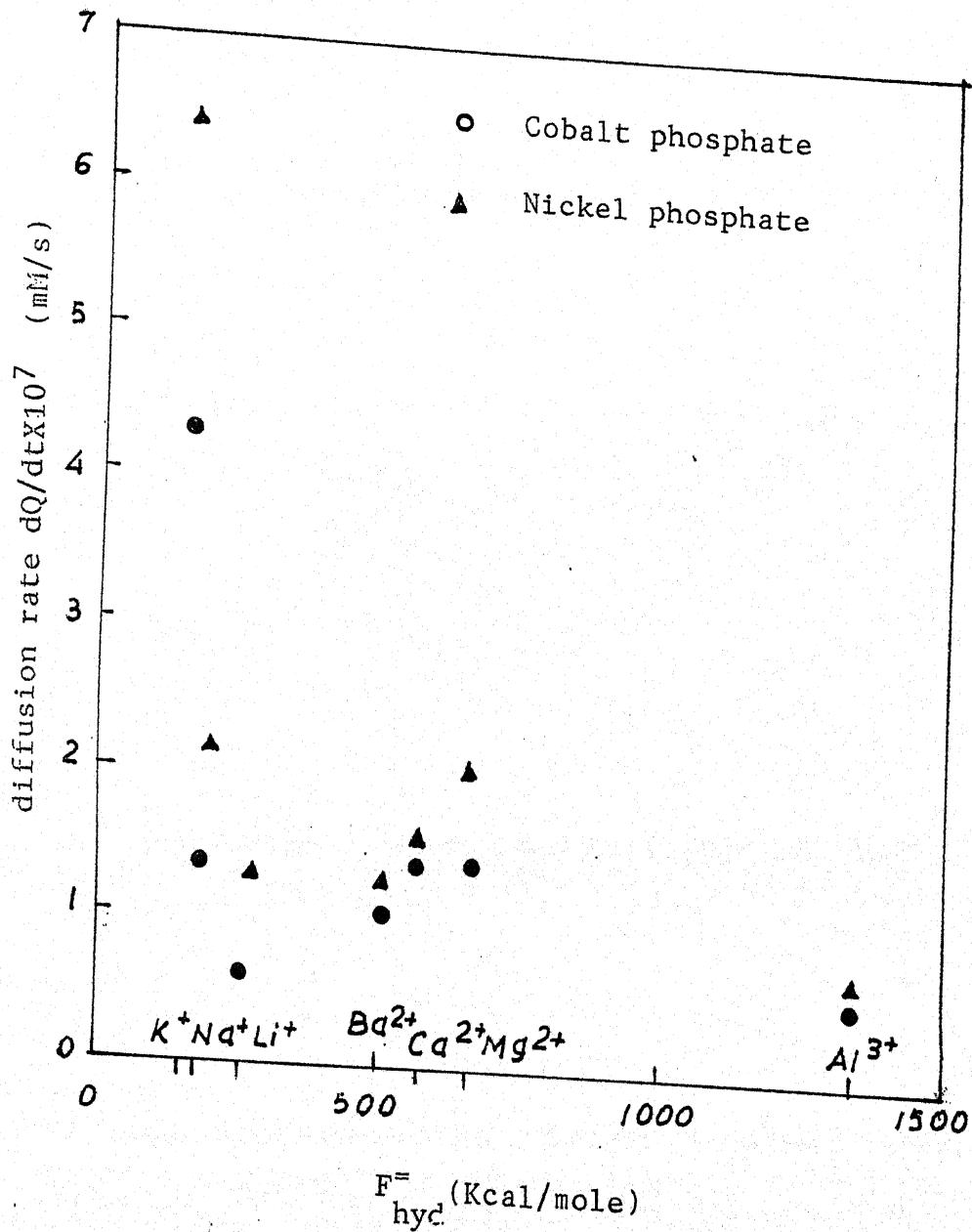


FIG. 28. Diffusion rate $dQ/dt \times 10^7$ (mM/s) at 25°C for various electrolytes (Chloride) through both the membranes plotted against free energy (F_hyd) of hydration of cations.

structure. That no such structural change is involved is evident from the linear plots of $\log dQ/dt$ versus $(1/T)$ given in Figs 29 and 30. The slope of these lines which is equal to $(Ea/2.303 R)$ gave the activation energy Ea required for the diffusion process. The values so derived are given in tables 31 and 32. The diffusion rate dQ/dt (millimol/h) is related to diffusion coefficient D (cm/sec) by the relation

$$\bar{D} = \frac{dQ}{dt} \times \frac{10^{-6}}{3.6} A \Delta C \quad (7)$$

where A is the membrane area (24.6 Cm^2) and ΔC is the difference in the electrolyte concentration existing across the membrane. Since area of membrane and concentration difference of the electrolytes are constants therefore D is proportional to dQ/dt and thus the slopes of linear plots of $\log \bar{D}$ vs $(1/T)$ and of $\log dQ/dt$ Vs. $(1/T)$ will be equal.

The theory of absolute reaction rate (45) has been applied to diffusion processes in membrane by several investigators (44-46, 62-64). According to Zolinsky et al. (44), we have

$$\bar{D} = \lambda^2 (KT/dh) \exp - F^* / RT \quad (8)$$

where K is Boltzman constant, d is. membrane thickness, h is plank constant, and λ is average distance between equilibrium positions in the process of diffusion.

ΔF^* is the free energy of activation for diffusion and is related to enthalpy ΔH^* and ΔS^* of activation of diffusion by Gibbs Helmholtz equation

$$\Delta F^* = \Delta H^* - T \Delta S^* \quad (9)$$

ΔH^* is related to Arrhenius energy of activation Ea by the equation

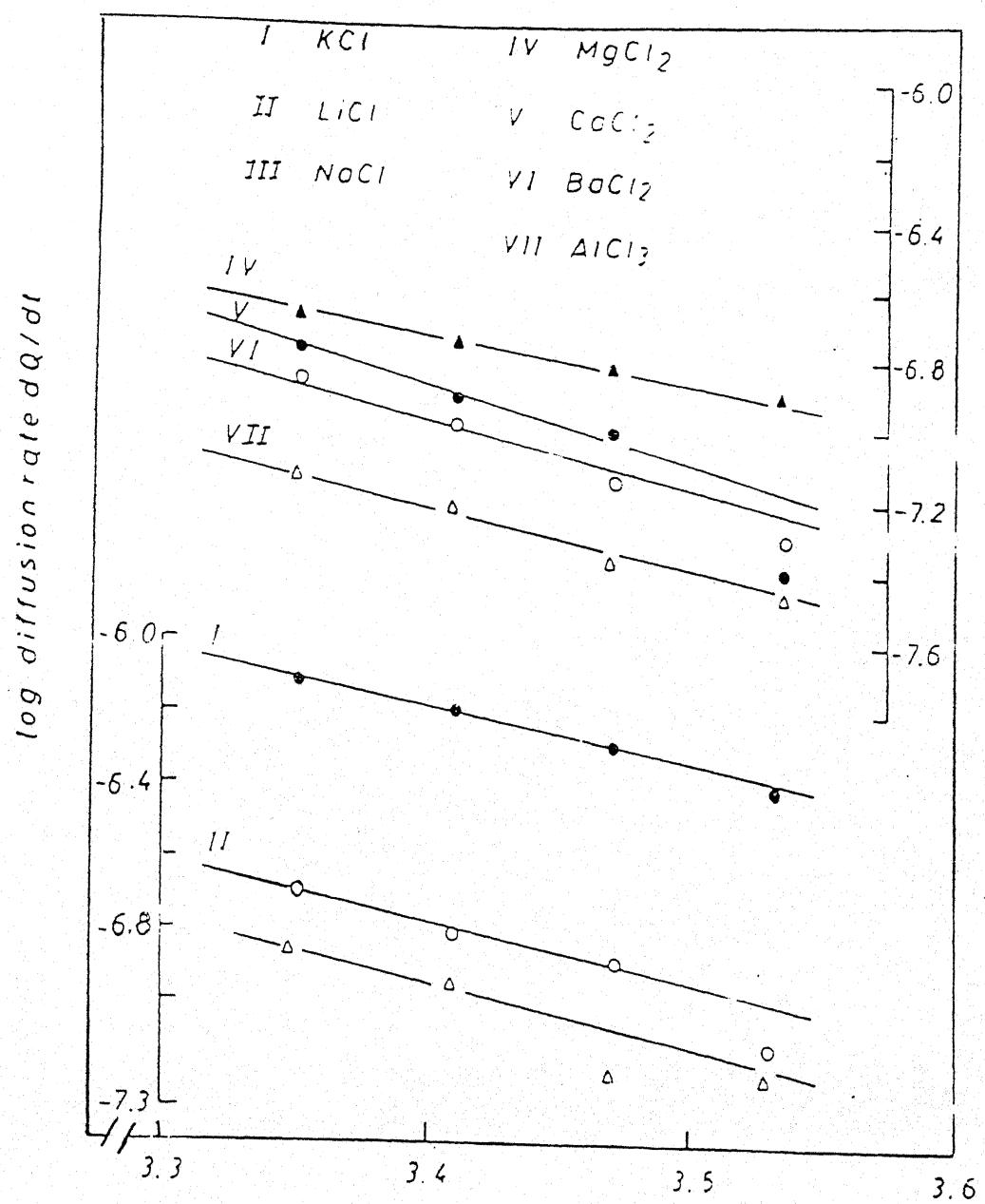


FIG. - 29

Plots of dQ/dt against $1/T$ for various electrolytes across cobalt phosphate membrane at 25°C

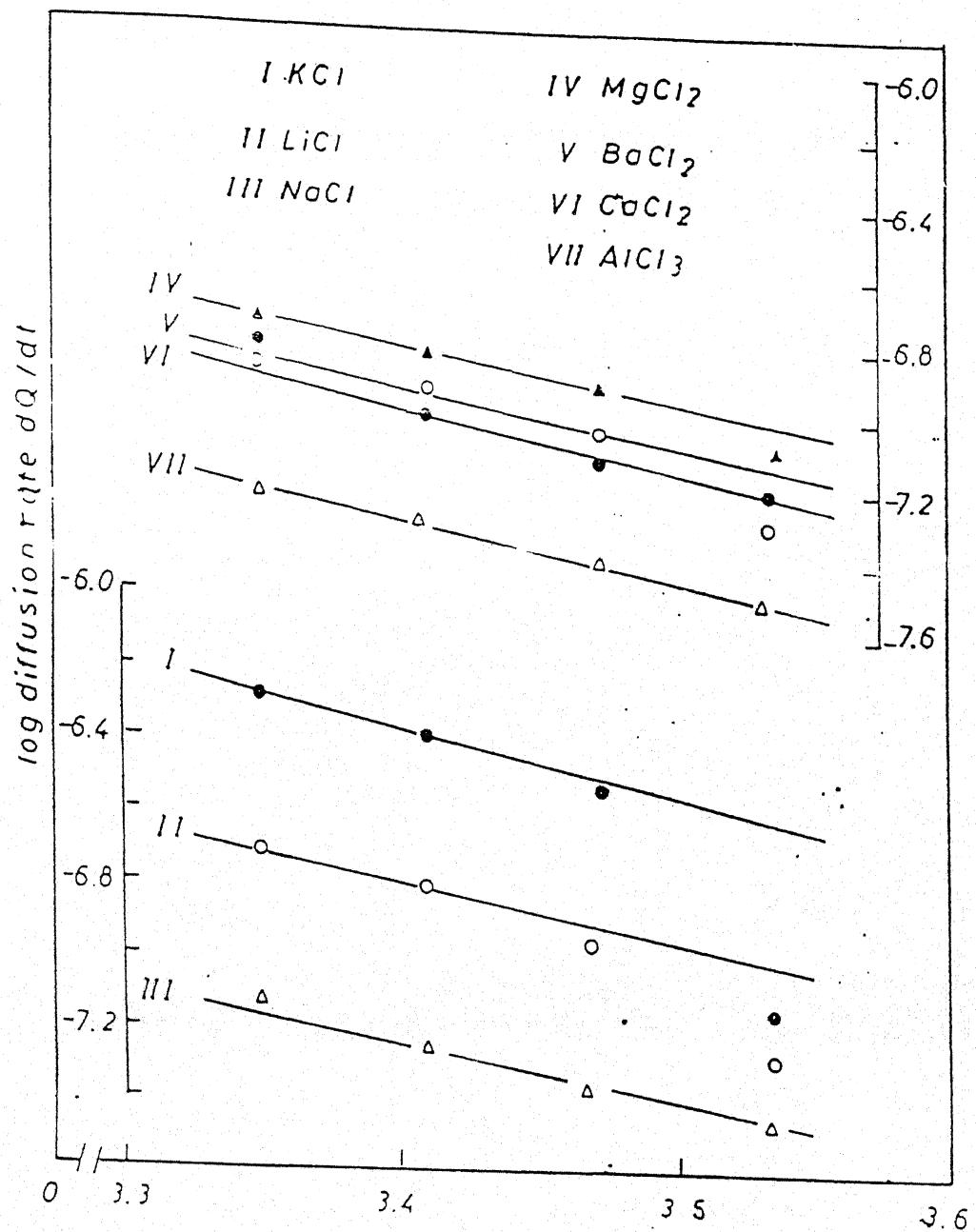


FIG.- 30

Plots of dQ/dt against $1/T$ for various electrolytes across Nickel phosphate membrane at 25°C

Table 31
 Experimental activation energy E_a and other Thermodynamic parameters
 calculated from transition state Theory of rate processes For Cobalt
 Phosphate Membrane at $25 \pm 0.1^\circ\text{C}$

Parameter Electrolyte	E_a (Kcal Mol ⁻¹)	$\Delta H \neq$ (Kcal Mol ⁻¹)	$\Delta F \neq$ (Kcal Mol ⁻¹)	$\Delta S \neq$ (e.u.)
KCL	7.40	6.80	11.00	-14.00
NaCl	6.70	6.10	11.30	-17.50
LiCl	6.40	5.80	11.80	-20.20
CaCl ₂	5.90	5.40	11.70	-21.40
BaCl ₂	6.10	5.50	11.90	-21.50
MgCl ₂	5.10	4.50	11.70	-24.50
AlCl ₃	4.90	4.30	12.40	-27.20

Table 32
 Experimental activation energy E_a and other Thermodynamic parameters
 calculated from transition state Theory of rate processes For Nickel
 Phosphate Membrane at $25 \pm 0.1^\circ\text{C}$

Parameter Electrolyte	E_a (Kcal Mol ⁻¹)	$\Delta H \neq$ (Kcal Mol ⁻¹)	$\Delta F \neq$ (Kcal Mol ⁻¹)	$\Delta S \neq$ (e.u.)
KCL	7.10	6.50	10.80	-14.30
NaCl	6.70	6.10	11.80	-19.20
LiCl	6.20	5.60	11.60	-20.00
CaCl ₂	5.90	5.30	11.70	-21.60
BaCl ₂	5.60	5.00	11.90	-23.40
MgCl ₂	5.50	4.90	11.60	-22.40
AlCl ₃	4.60	4.00	12.30	-27.80

Vide Figs. 31 - 33

$$\Delta H^\ddagger = Ea - RT \quad (10)$$

As the values of d and of the universal constants are known, values of, ΔH^\ddagger , ΔS^\ddagger , and ΔF^\ddagger can be calculated provided the value of λ is, known. Different investigators (44-46,63,65) have used values ranging from 1.5 A^0 for λ . In this work a value of 1 A^0 has been used in calculations, and the values so derived for the different thermodynamic parameters are given in Tables 31 and 32. For purpose of comparison, in Table 33 are given the values of ΔS^\ddagger determined by various investigators for a variety of systems. The values of ΔS^\ddagger (see Table 33) are either positive or negative for membranes. There are few values which are close to zero and correspond to liquid systems. According to Eyring and co-workers (44,45), the values of ΔS^\ddagger indicate the mechanism of flow; large positive ΔS^\ddagger is interpreted to reflect breakage of bonds, while low values indicate either formation of covalent bond between the permeating species and membrane material or that the permeation through the membrane may not be rate determining step.

On the contrary, Barrer (63,66,67) has developed the concept "zone activation" and applied it to the permeation of gases through polymer membranes. According to this zone hypothesis, a high ΔS^\ddagger , which has been correlated with high energy of activation for diffusion, means either the existence of a large zone of activation or the reversible loosening of more chain segments of the membrane. A low ΔS^\ddagger , then means either a small zone of activation or no loosening of the membrane structure on permeation. In view of these differences in the interpretation of ΔS^\ddagger , Shuller et al. (46), who found negative ΔS^\ddagger value for sugar permeation through collodion

Table 33
 Thermodynamic Parameters ΔS^* For permeation of various substances
 Through different systems.

Diffusing Species	Diffusion system Medium	Entropy factor $\lambda [e\Delta S^* / R]^{1/2}$ A	ΔS^* , e.u.	Reference
Water	Water	10.0	8.5	
Phenol	Methyl alcohol	0.4	0.3	
Phenol	Benzene	0.4	0.3	31b
$C_2H_2Br_4$	$C_2H_2Cl_4$	0.00	0.00	
Bromine	CS_2	0.4	-2.6	
Mannitole	Water	1.8	3.1	50b ^b
H_2	Butadiene-acrylonitrile Membrane	181	15.0	
N_2	Butadiene-acrylonitrile Membrane	129	13.7	
N_2	Butadiene-methyl meth-acrylate Membrane	149	14.3	31 ^b 52 ^c
Ar	Butadiene-methyl meth-acrylate Membrane	92	12.4	
N_2	Butadiene-polystyrene Membrane	23	6.8	
Ar	Butadien-polystyrene Membrane	32	8.3	
H_2	Neoprene Membrane	73	11.4	
N_2	Neoprene Membrane	214	15.7	31 ^b 52 ^c
Ar	Neoprene Membrane	184	15.2	
H_2	Chloroprene Membrane	149	14.3	
H_2	Silicone rubber Membrane (Sheet)	0.3	-2.4	
N_2	Silicone rubber Membrane (Sheet)	0.84	-4.0	
O_2	Silicone rubber Membrane (Sheet)	0.60	-5.3	53
He	Silicone rubber Membrane (Sheet)	0.86	-4.9	
Ar	Silicone rubber Membrane (Sheet)	0.82	-4.1	
H_2	Glass Membrane	4×10^{-2}	-16.1	
He	Glass Membrane	4×10^{-2}	-16.1	32
Sucrose	Collodion Membrane	1.1×10^{-2}	-22.2	
Lactose	Collodion Membrane	4.3×10^{-2}	-16.8	
Mannitol	Collodion Membrane	8.1×10^{-3}	-23.4	32
Raffinose	Collodion Membrane	2.4×10^{-2}	-19.1	
H_2O (Source Solution)	Collodion Membrane	1.2×10^{-2}	-21.8	
H_2O	n-Hexadecane liquid	2.8	-0.2	55
H_2O	Hexamethyltetracoson	4.8	1.9	

	liquid				
H ₂ O	Polyethylene Membrane	3.9x10 ³	28.4	56	
H ₂ O	Polyethylene Membrane	25x10 ³	35.8		
H ₂ O	Liquid bilayer	5.5x10 ⁻²	-15.8	51	
	Membrane (Oxidized cholesterol)				
H ₂ O (Endo- osmosis)	Arbacia eggs (unfertilised)	14.4x10 ³	3.16		
Propionamide	Arbacia eggs (unfertilised)	26.9x10 ³	34	30 ^d	
Butyramide	Arbacia eggs (unfertilised)	12.1x10 ⁴	40		
Nonelectrolyte (glycerol, glycols thiourea)	Oxerythrocyte Membrane	77	3.7	50 ^b	

a All results correspond to $\lambda = 3 \text{ \AA}^0$ unless otherwise noted

b Calculations correspond to $\lambda = 31 \text{ \AA}^0$

c Calculations correspond to $\lambda^2 = 10^{-15} \text{ cm}^2$

d Calculations correspond to $\lambda = 5 \text{ \AA}^0$

membrane, have stated that "it would probably be correct to interpret the small negative value of ΔS^\ddagger mechanically as interstitial permeation of the membrane (minimum chain loosening) with partial immobilization in the membrane (small zone of disorder)". On the other hand, Tien and Ting (65) who found negative ΔS^\ddagger values for the permeation of water through very thin (50 \AA° thickness) bilayer membrane, stressed the possibility that the membrane may not be the rate-determining step. Based on additional experimental data, they come to the conclusion that the solution-membrane interface was the rate-limiting step for permeation.

The result of our investigations, Table 31 and 32 indicate that electrolyte permeation gives rise to negative values for ΔS^\ddagger for both the membranes show the similar behaviour for different electrolytes. It is in general found that as the valence of the individual ion is increased, the decrease in the value of ΔS^\ddagger is enhanced.

Since the membranes used in this study are fairly thick compared to bilayers. It is believed that the membrane alongwith solution-membrane interface controlled the electrolytes permeation with partial immobilization in the membrane, the partial immobility increasing in a relative manner with increase in the valence of the ion constituting the electrolyte.

In Figs. 31-33, the individual ionic distribution to the property of aqueous ions given by Noyes (68): namely $\Delta H_{\text{hydration}}$, $\Delta F_{\text{hydration}}$, $\Delta S_{\text{hydration}}$ Li^+ , Na^+ , K^+ as well as those of Ba^{2+} , Ca^{2+} and Mg^{2+} are plotted against the corresponding ΔH^\ddagger , ΔS^\ddagger , and ΔF^\ddagger values for diffusion through the membranes. It is found that at least some formal relationship exists between these thermodynamic parameters.

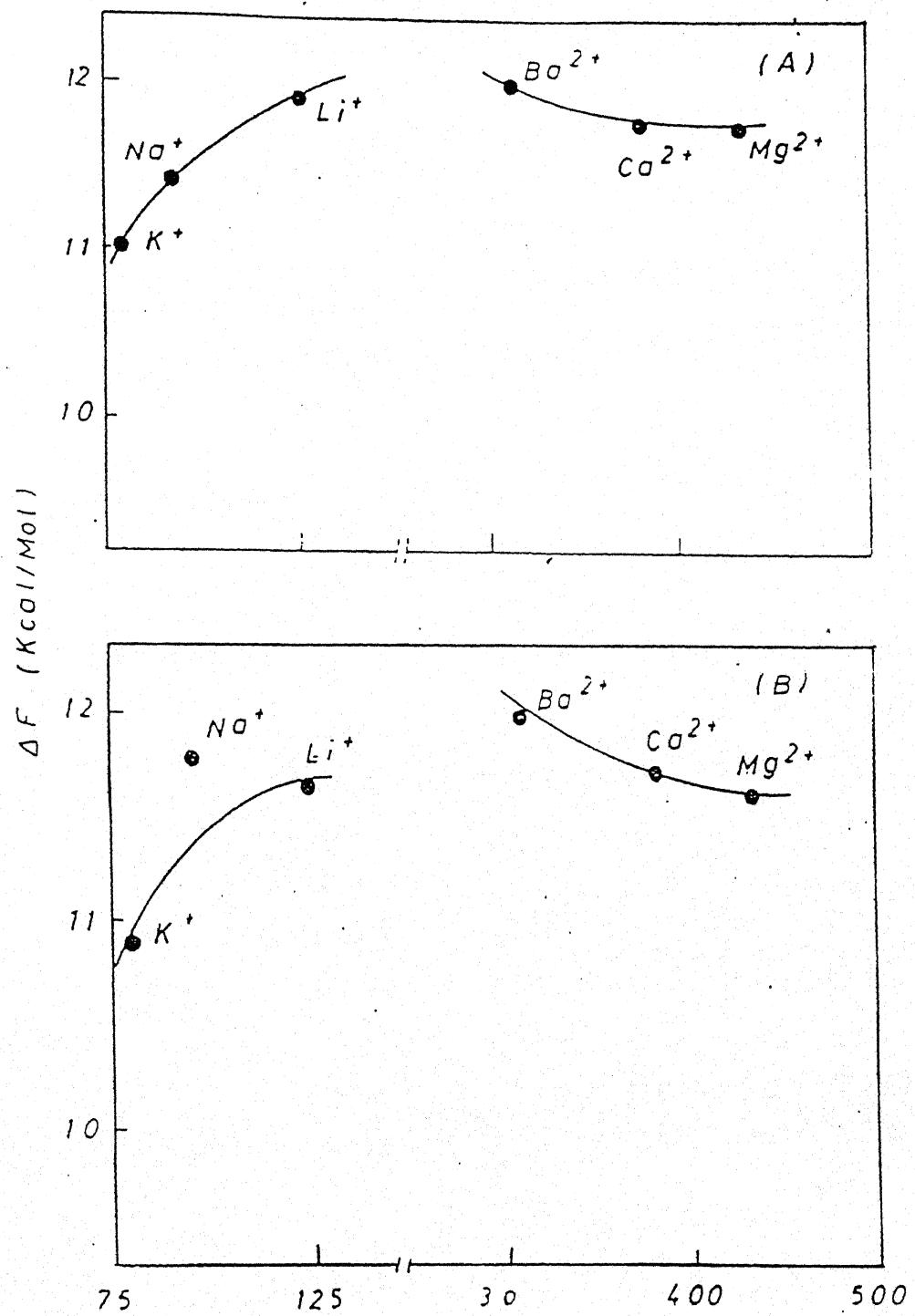


FIG. - 31

Plots of ΔF (Kcal/Mol) for the diffusion of various electrolytes (at 25°C) against ΔHyd (Kcal/Mol) for respective cations through (A) Cobalt phosphate and (B) Nickel phosphate membranes

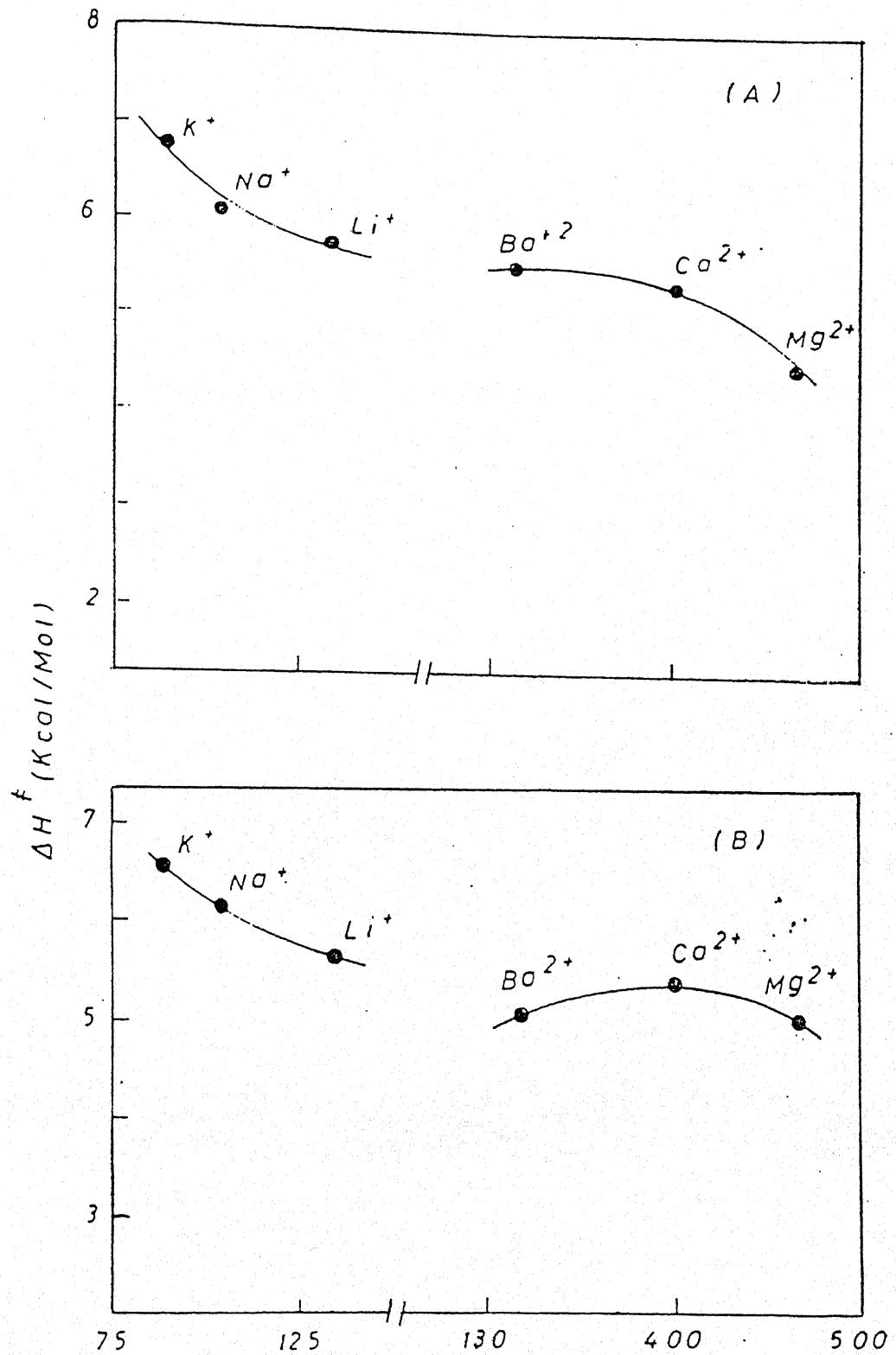


FIG.- 32

Plots of ΔH_f (Kcal/Mol) for the diffusion of various electrolytes (at 25°C) against ΔH_{hyd} (Kcal/Mol) for respective cations through (A) Cobalt phosphate and (B) Nickel phosphate membranes

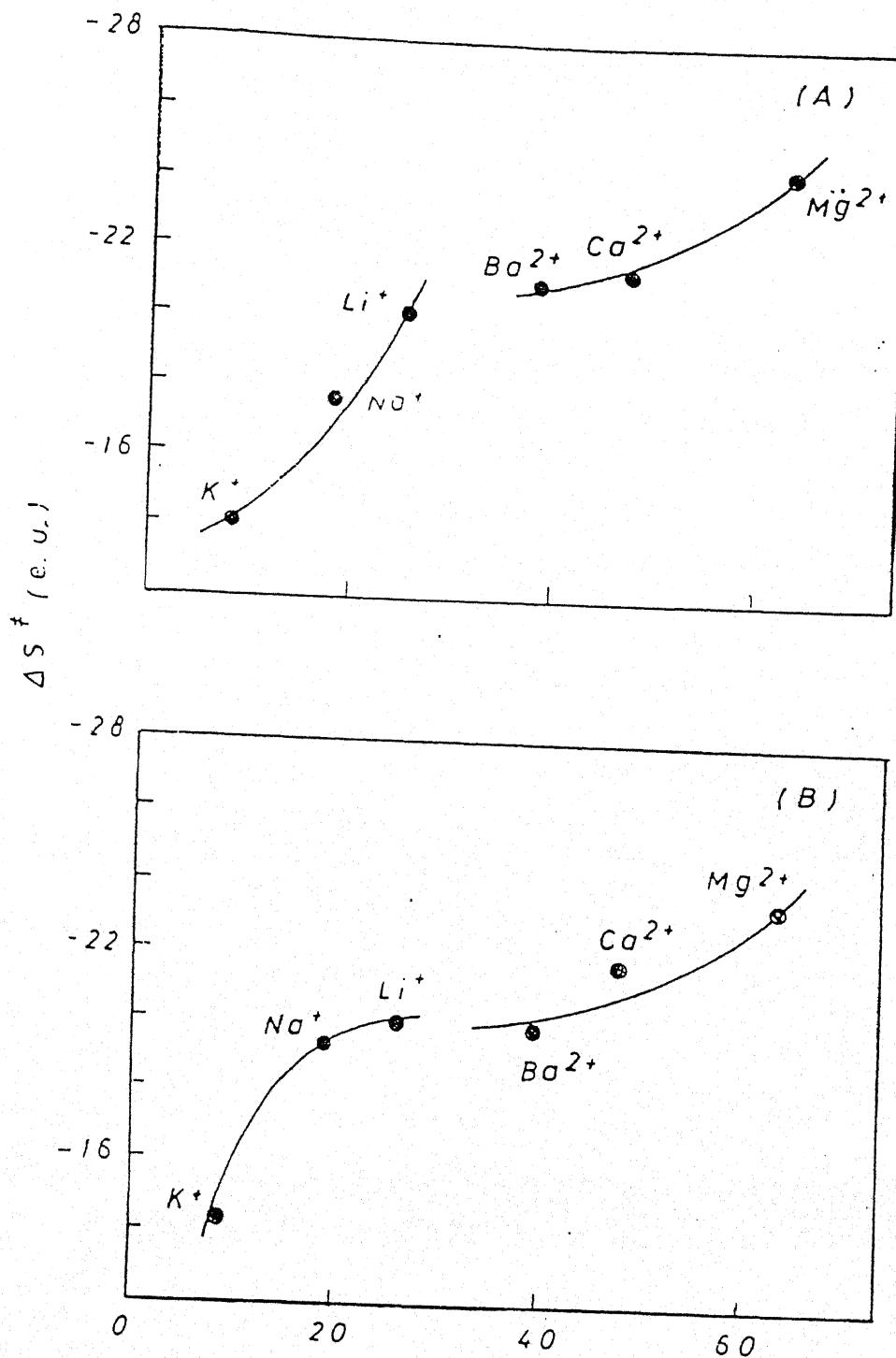


FIG.- 33

Plots of ΔS° (e.u.) for the diffusion of various electrolytes (at 25°C) against ΔH° (Kcal/Mol) for respective cations through (A) Cobalt phosphate and (B) Nickel phosphate membranes

REFERENCES

1. P.H. Abelson, Science, 224, 1421 (1989).
2. R.A.W. Dryfe, A.O. Simm, B. Kralji, J. Am. Chem., Soc., 125, 13014, (2003).
3. W.J. Petzyn, J.A. Quinn, Science 166, 751, (1969).
4. A.K. Banga, S. Bosa, T.K. Ghosh, Int. J. Pharm. 179, 1, (1999).
5. T.Y. Cath, V.D. Adams, A.E. Childress, J. Membrane. Sci. 228, 5, (2004).
6. G.J. Hills, P.W.M. Jocabs and N. Lakshminarayanaiah, Nature, 179, 96 (1957).
7. Y. Kobalake; Bull. Tokyo Inst. Technol. Ser. B. P. 97 (1959).
8. H.Z. Friedlander and R.N. Rickles, Anal. Chem., 37, 27A (1965); Chem. Eng., 73, 111 (1966).
9. R.N. Rickles and H.Z. Friendlander, Intern. Sci. Technol., 30 (7), 53 (1966).
10. N. Lakshminarayanaiah, Transport Phenomena in Membrane, Academic Press, New York (1969); Membrane Electrodes, Academic. Press New York (1976).
11. N. Lakhshminarayanaiah, Membrane Electrodes, Academic Press, New York (1976).
12. S. Glasstone, An introduction to electrochemistry Affiliated East west Press, New Delhi (1971).
13. R.E. Kesting "Synthetic Polymer Membranes" Mc Graw Hill, Book company, New Delhi (1971).

14. R.D. Noble and S.A. Stern, *Membrane Separation Technology*, Elsevier, New York (1995).
15. F. Helfferich, "Ion Exchange" Mc Graw Hill, New York (1962).
16. R. Schlogl; : *Stoff transport Durch Membrane* Steinkopff, Darmstadt (1964); *Fort Scr. Physik, Chem.* 9 (1964).
17. E. Samson and J. Marchand, *J. Colloid and Interface science*, 215, 1 (1999).
18. F. Takashi and A. Yamacurchi, *Bull. Chem. Soc. Jpn.* 73, 2732 (2000).
19. Armin Kargol, *J. Membrane Science*, 174, 43 (2000).
20. Z. Polaty and A. Zakora, *J. Membrane Science*, 173, 211 (2000).
21. G. Hoch, A Chauhan and C.J. Radke, *J. Membrane Science*, 214, 199 (2003).
22. T. Teorell, in "Membrane Phenomena", *Discuss. Faraday Soc.*, 21, 9 (1956).
23. N. Lakshminarayanaiah and F.A. Siddiqi, *Biophys. J.*, 11, 603, 617 (1971).
24. N. Lakshminarayanaiah and F.A. Siddiqi, *Biophys. J.*, 12, 540 (1972).
25. N. Lakshminarayanaiah and F.A. Siddiqi in "Membrane Process in Industry" ed. By Bier, Plenum Publishing Corporation, New York (1971).
26. N. Lakshminarayanaiah and F.A. Siddiqi, *J. Polm. Sci.*, 8, 2949 (1970).
27. N. Lakshminarayanaiah and F.A. Siddiqi, *Z. Phys. Chem., Phys. Chem.*, (Frankfurt), 78, 150 (1972).

28. A.M. Liquori and L. Botre, Ric, Sci., 34,6, (1964).
29. A.M. Liquori and L. Botre, J. Phys. Chem., 71, 3765 (1967).
30. M.N. Beg, F.A. siddiqi, R.S. Kushwaha and I. Altaf, J.E. Electroanal. Chem, 89, 141 (1978).
31. R.S. Kushwaha, M.A. Ansari, N. Akhtar and P. Singh, Indian Journal of Chemistry, 31A, 439 (1992).
32. R.S. Kushwaha, A. Kumar and R.B. Sharma, Flora and Fauna, Vol., 7, 9 (2001).
33. R.S. Kushwaha, M.A. Ansari and R. Tiwari, Ind- J. Chem., 40 a, 270 (2001).
34. R.S. Kushwaha, M.A. Ansari and A- Bhartiya, J. Chemical and environment Research, 12 (3 & 4) (2003).
35. M.A. Ansari, R.S. Kushwaha, A.K. Verma and C.M. Gupta, U. Scientist Phyl. Sciences, Vol, 8, No 1, 19 (1996).
36. M.A. Ansari, M. Kumar and R.S. Kushwaha. J. Ind. Council of Chemist, Vol. 23, No. 1, 31 (2006)
37. M.A. Beg and M.A. Matin, J. Membrane Science, 196, 95 (2002).
38. R.S. Kushwaha, M.A. Ansari and S. Agrawal Vol., 21, No. 2, 10, (2004)
39. O. Kedem and A. Katchalsky, Trans. Faraday Soc., 71, 3765 (1967).
40. R. Schlogl, Discuss Faraday Soc., 21, 46 (1956).
41. G. Eisenman, in "Membrane Transport and Metabolism," ed. by A. Kleinzeller and A. Kotyk, Academic Press, New York, 163 (1961).
42. G. Eisenman "The Glass Electrode", Inter Science Publishers, Inc., New York (1965).
43. G. Eisenman, Biophys. J. Suppl., 2, 259 (1962).

44. B.J. Zwolinski, H. Eyring and C.E. Reese; *J. Phys. Chem.*, 53, 1426 (1949).
45. S. Glasston, K. J. Laidler and H. Eyring, "the Theory of Rate Process", Mc Graw - Hill, New York, P. 525, 544 (1941).
46. E.K. Shuller, C.A. Dames and K.J. Laidler, *J. Chem. Phys.*, 17, 860 (1949).
47. R. Schlogl, *Bor, Bumsluges Phys., Phys. Chem.*, 70, 400 (1966).
48. W.W. Kittelberger, *J. Phys. Colloid Chem.*, 53, 3925 (1949).
49. V. Subrahmanyam and N. Lakshminarayanaiah, *J. Phys. Chem.* 72, 4314 (1968).
50. H.P. Gregor, Research and development Report No. 193, Office of Saline water, U.S. Department of the interior, Washington, D.C. May (1966).
51. Sherry, "Ion Exchange", Editor, J.A. Marinsky, Dekker, New York , 2, (1968).
52. N.W. Rosenberg, J.H.B. George, and W.D. Potter, *J.Electrochem. Soc.*, 104, 11 (1957).
53. G.Z. Schulz, *A. Inorg. Anal. Chem.*, 97, 301 (1959).
54. J. Teorell, *Proc. Soc. Exptl. Biol.*, 33, 282 (1935); *Proc. Natl. Acad. Sci., (USA)*, 21, 152 (1935); *Progr. Bio Phys. Chem.*, 3, 305 (1953).
55. K.H. Meyer and J.F. Sievers, *Helv. Chem. Acta.*, 19 649, 605, 987 (1936).
56. K. Sollner, *J. Phys. Chem.*, 49,47, 171 (1945); *J. Electrochem. Soc.*, 97, 139 (1950); *Ann. N.Y. Acad. Sci.*, 57, 177 (1953).
57. D. He, M. Ma and Z. Zhao, *J. Memb. Science*, 168, 53 (2000).

58. Z. Paloty, and A. Zakova, *J. Memb. Science*, 173, 211 (2000).
59. G. Hoch, A. Chauhan and C.J. Radice, *J. Membrane Science*, 214, 199 (2003).
60. P.S. Pollabandi and D.M. Ford; *J. Memb. Sci.*, Vol., 171, 2 (2000).
61. A. Hirateuka, H. Muguruma, R. Nagata, R. Nakamura and K. Sota, S. Uchiyanma and I. Karube, *J. Memb. Sci.*, 175, 25 (2000).
62. Y. Marcus and A.S. Kerter, *Ion Exchange and Solvent Extraction of metal complexes*, In teoscience, New York, P. 13 (1959).
63. R.M. Barrer, *Trans. Faraday Soc.*, 38, 322 (1942).
64. W.D. Stien, *The movement of molecules across cell membranes*, Academic Press, New York, (a) PP. 70-89 (b) P. 89 (1967).
65. H.T. Tien and H.P. Ting, *J. Colloid Interface Sci.*, 27, 702 (1968).
66. R.M. Barrer and G. Skirrow, *J. Polymer Sci.*, 3, 549 (1948).
67. R.M. Barrer and H.T. Chio, In "Transport Phenomena in Polymeric Films", (*J. Polym. Sci. c*, 10), C.A. Kumins, Ed., Interscience, New York, P. 111 (1962).
68. R.M. Noyes, *J. Am. Chem. Soc.*, 84, 513 (1962).

Chapter : III

*Bi-ionic
Potential
Studies*

INTRODUCTION

When two electrolyte solution of the same concentration are placed, one on either side of a membrane, diffusion of cations and anions through the membrane takes place. In dilute solutions, as the ionic activities are almost equal, each ion moves through the membrane following the order of their mobilities observed in dilute aqueous solutions. through the membrane following the order of their mobilities observed in dilute aqueous solutions. But their absolute values in the membrane will be lower. if the membrane is a charged one, the co-ions are excluded from the membrane phase and only the counterions diffuse through the membrane. A quantitative description of the phenomena arising across an ion-exchange membrane when two different counterions (bi-ionic) or more (multiionic) diffuse through the membrane is given by Helfferich (1). A steady electromotive force of a bi-ionic cell containing two electrolytes. AP and BP separated by a membrane is called the bi-ionic potential (BIP). This potential is a measure for the selectivity of a membrane for the ions of the same sign and has been the subject of many theoretical and experimental studies, but it appears that no. Satisfactory results have as yet been established. The Mathematically rigorous equations were derived on the basis of the thermodynamics of irreversible processes by Helfferich (1) and Scatchard (2). In their derivations, however, they considered only a perfectly. cation-selective (anion-selective) membrane separating. Two mixtures of uni-univalent electrolytes with a common anion (cation), i.e., the neglected the effect of flow of anion on the BIP. Moreover,

these type of the treatment did not provided information about the actual mechanism which produces observed BIP.

We are engaged in the study of membranes (4-17) which can serve as models for biological systems (18), particularly parchment membranes which in some formal aspects at least, according to Teorell (19) behave exactly like gastric mucosal membranes. Membrane theories of Teorell (19), Meyer and Sievers (20), Schmid (21), Sollner (22), Gregor (23), Eisenman (24) and Sherry (25), etc. have been applied for the evaluation of various parameters. Recently the work of Kedem and Katchalsky (26), Spiegler (27), Scatchard (28), Helfferich (29), Schlogl (30), Kobatake et al. (31-34) etc. based on non-equilibrium thermodynamics has been applied to elucidate the mechanism of transport through parchment supported (1-10) and polymeric composite membranes (13-17). This chapter deals with the application and test of the most recent theories of membrane potential developed by Nagasawa et al. (35,36) based on the thermodynamics of irreversible processes as well as those of Toyoshima and Nozaki (37) on bi-ionic potential.

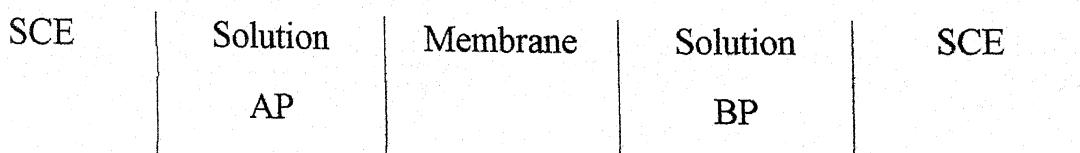
EXPERIMENTAL

The membranes of Nickel Phosphate and Cobalt Phosphate were prepared by the method of interaction suggested by Kushwaha and Co-worker (10).

The electrochemical cell of the type

SCE		Solution		Membrane		Solution		SCE
		C_1				C_2		

was used for measuring electrical potentials arising across the membrane by maintaining a tenfold difference in concentration (i.e. $C_2/C_1 = 10$) and using a Pye Precision Vernier potentiometer (No. 7568). The bi-ionic potentials were measured by setting up an electrochemical cell of the following type



and keeping the concentration of both AP and BP electrolytes the same. The various salt solutions (chloride and nitrate of K^+ , Na^+ , Li^+ and NH_4^+) were prepared from analytical grade reagents (B.D.H.) by using deionized water. In both the measurements of membrane potential and bi-ionic potential the solutions were vigorously stirred and temperature was maintained at 25°C. The parchment paper was supplied by Baird and Tatlock Ltd. (London).

RESULTS AND DISCUSSION

The membrane potential data obtained with nickel phosphate and Cobalt Phosphate parchment supported membranes using various 1 : 1 electrolytes are plotted as a function of $\log((C_1 + C_2)/2)$ with the ratio $v (= c_2/c_1)$ fixed at 10. These plots are shown in Fig. 1.

Tasaka et al. (36) derived a general equation for membrane potential existing across a negatively charged membrane. In the limit of high electrolyte concentrations they found the following approximate form as:

$$-\Delta\phi_m = (RT/F)[v/(v-1)](X/2)1/c_1 + \dots \quad (1)$$

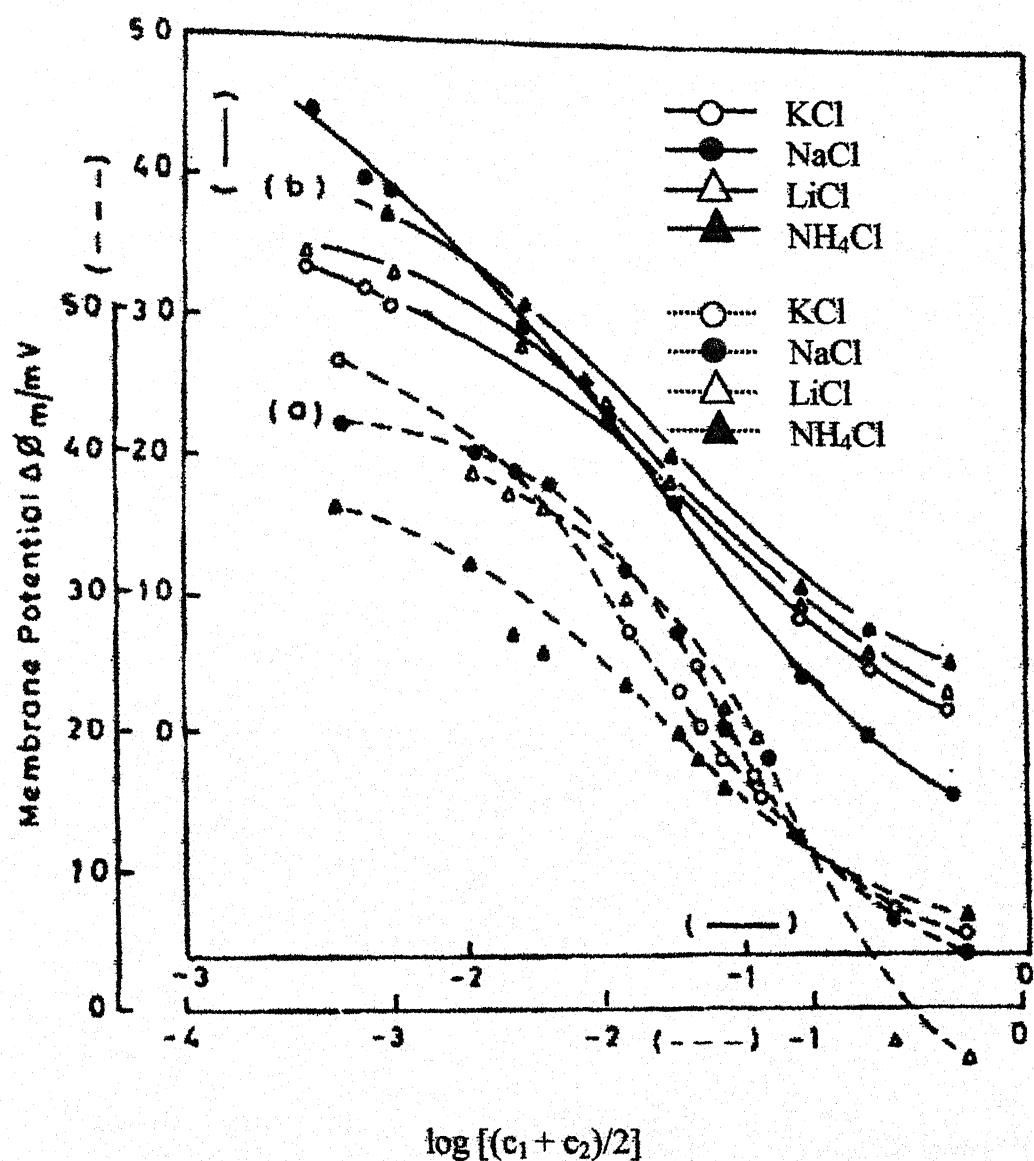


Fig.1. Plots of membrane potentials $\Delta\phi_m$ vs. $\log (c_1 + c_2)/2$ for (a) cobalt phosphate and (b) nickel phosphate membranes in contact with various 1:1 electrolyte solutions at 25°C.

where X is the concentration of fixed charge on the membrane. Equation (1) predicts a relationship between $\Delta\phi_m$ vs. $1/c_1$ from which X can be calculated. Figures 2 and 3 show plots between $\Delta\phi_m((v-l)/v)$ vs. $1/c_1$. The tangents from which the slopes are evaluated are shown by the dotted lines. The values of charge densities X obtained from the various slopes are given in Table 1 and 2 with different electrolytes.

The transport number was calculated using Hersh's equation (38)

$$\bar{T}_c = (\bar{U}/\bar{V})\bar{c}_+ / (\bar{U}/\bar{V})\bar{c}_+ + \bar{c}_- \quad (2)$$

where (\bar{U}/\bar{V}) is the mobility ratio in the membrane phase and \bar{c}_+ and \bar{c}_- have been calculated using the expression given by Hersh (38)

$$\bar{c}_+ = \frac{1}{2} \left(\sqrt{(X)^2 + 4c_1^2} + X \right) \quad (3a)$$

$$\bar{c}_- = \frac{1}{2} \left(\sqrt{(X)^2 + 4c_1^2} - X \right) \quad (3b)$$

The transport number of the counter ions in the membrane phase was calculated using eqn. (2) by substituting the value of X and (\bar{U}/\bar{V}) from Table 1 and 2 are given in Table 3 and 4 for two membranes with different electrolytes.

BI-IONIC POTENTIAL (BIP)

A steady electromotive force of a bi-ionic cell containing two electrolytes AP and BP separated by a membrane, is called bi-ionic potential

TABLE-1

Comparison of Charge Density for Different Membrane-Electrolyte Systems of Nickel Phosphate Membrane.

Electrolyte	TMS (19,20)		Kobatake et al. (31)	Tasaka et al. (36)
	\bar{U} / \bar{V}	$\times 10^3$ eq/l	$\times 10^3$ eq/l	$\times 10^3$ eq/l
KCl	1.4	1.8	3.2	1.2
NaCl	1.4	1.5	3.5	1.9
LiCl	1.0	2.1	3.2	2.2
NH ₄ Cl	1.4	2.2	3.4	2.1

TABLE -2

Comparison of Charge Density for Different Membrane Electrolyte System of Cobalt Phosphate Membrane.

Electrolyte	TMS (19,20)		Kobatake et al. (31)	Tasaka et al. (36)
	\bar{U} / \bar{V}	$\times 10^3$ eq/l	$\times 10^3$ eq/l	$\times 10^3$ eq/l
KCl	1.0	1.9	4.1	1.4
NaCl	1.2	2.1	3.4	1.5
LiCl	1.0	2.6	3.2	1.4
NH ₄ Cl	1.0	2.9	3.1	1.9

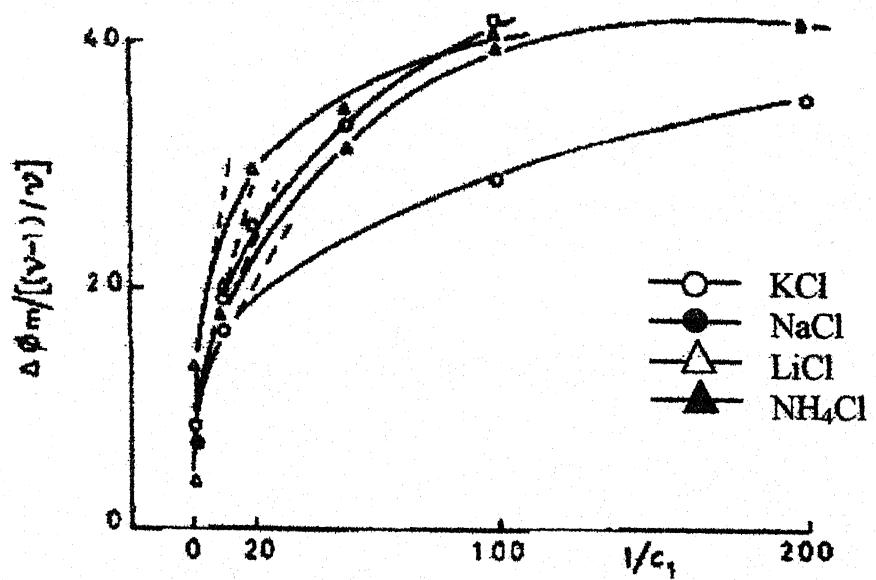


Fig. 2 Plots of $\Delta\phi_m/(v-1)/v$ vs. $1/c_1$ for various electrolyte with cobalt phosphate membrane.

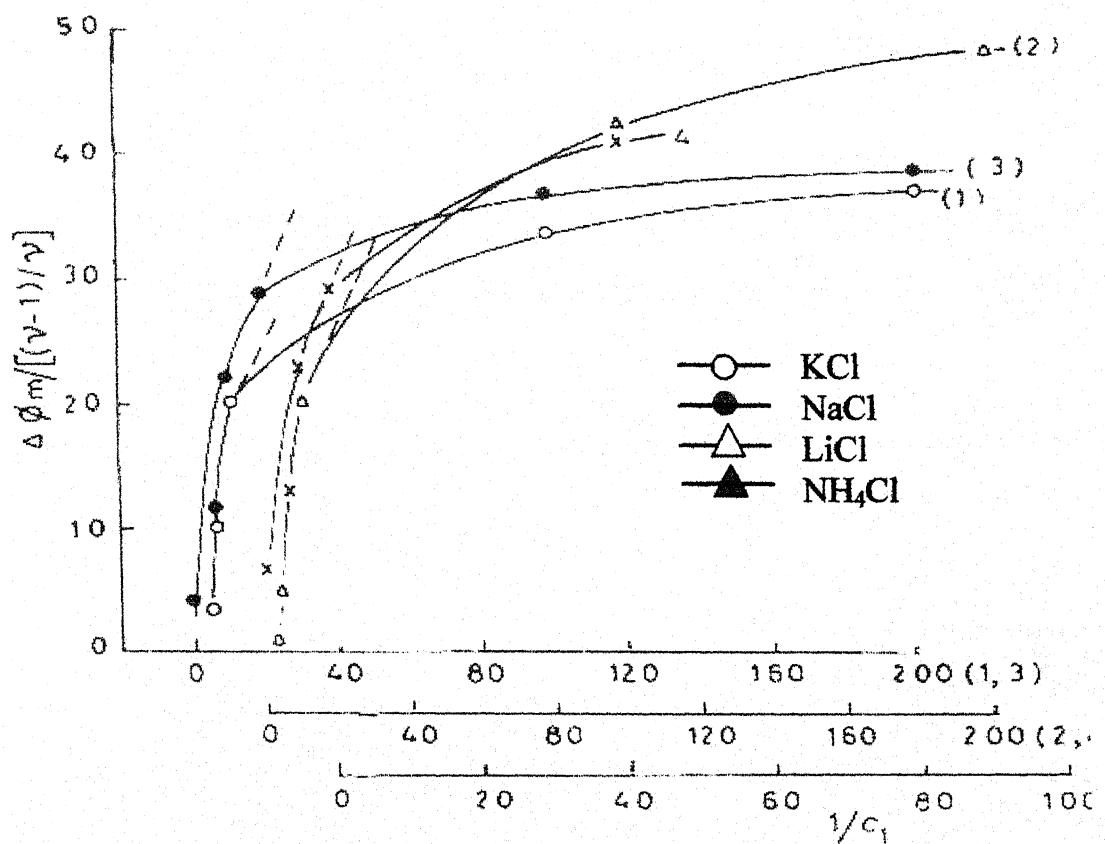


Fig. 3 Plots of $\Delta\phi_m / [(v-1)/v]$ vs. $1/c_1$ for various electrolyte with nickel phosphate membrane.

TABLE-3

Transport Number of Counter Ions as a Function of External Electrolyte Concentration for Nickel Phosphate Membrane.

Electrolyte	Concentrations/mol dm ⁻³					
	1.0	0.5	0.1	0.05	0.01	0.001
KCl	0.58	0.59	0.60	0.61	0.73	0.97
NaCl	0.58	0.58	0.68	-	0.70	0.98
LiCl	0.50	0.51	0.55	0.59	0.85	0.99
NH ₄ Cl	0.58	0.59	0.60	0.62	0.76	0.99

TABLE-4

Transport Number of Counter Ions as a Function of External Electrolyte Concentration for Cobalt Phosphate Membrane

Electrolyte	Concentrations/mol dm ⁻³					
	1.0	0.5	0.1	0.05	0.01	0.001
KCl	0.50	0.51	0.57	0.63	0.91	0.98
NaCl	0.55	0.55	0.56	0.60	0.70	0.98
LiCl	"0.51	0.52	0.58	0.66	0.92	0.99
NH ₄ Cl	0.51	0.52	0.54	0.71	0.94	0.99

(BIP). This potential is a measure of selectivity of a membrane for ions of the same sign. Various mathematically rigorous equations have been derived on the basis of thermodynamics of irreversible processes by Scatchard (28) and Helfferich (29). Biionic potentials have also been reported by Michaelis (39), Marshall and Krinbill (40), Meyer and Bernfeld (41), Sollner et al. (42), Manecke (43) and Wyllie (44), etc. Recently Toyoshima and Nozaki (37) have derived the equation for BIP and membrane potential on the basis of non-equilibrium thermodynamics, using the appropriate assumptions for the mobilities and activity coefficients of small ions in the membrane phase which is applied here to our system of parchment supported membranes.

They considered a system in which two large compartments contain the aqueous solutions composed of two simple 1:1 electrolytes AP and BP. Here A and B represent the cationic species and P is the common anion. The electric charges carried by the membrane matrix are negative charges and are distributed uniformly with a charge density X . They showed that the apparent transport number of the anion is approximately given by (their eqn. 36)

$$1/t_- = V_N + (V_N - 1)[(v - 1)/v \ln v] X(X/K_N) 1/c_N^I \quad (4)$$

where

$$V_N = 1 + u_N^o / u_p^o, \quad (5)$$

U^o are the limiting mobilities and K_N is defined by

$$K_N^2 (a_{NP})_I^2 = (a_N)_O (a_P)_O$$

$$K_N^2 (a_{NP})_{II}^2 = (a_N)_L (a_P)_L \bar{c}_+ \quad (6)$$

where $(a_{NP})_I$ and $(a_{NP})_{II}$ are the mean activities of the electrolyte NP ($N = A$,

B) in both solution I and II, respectively, defined by

$$\begin{aligned} (a_{NP})_I^2 &= a_N^I a_P^I \\ (a_{NP})_{II}^2 &= a_N^{II} a_P^{II} \end{aligned} \quad (7)$$

$(a_i)_0$ and $(a_i)_L$ ($i = A, B, P$) are the single ion activities of species i in the membrane phase at $X = 0$ and $X = L$ and K_N ($N = A, B$) is defined by

$$1/K_N = \exp(\mu_N^{O^m} - \mu_N^{O^b} - \mu_P^{O^m} - \mu_P^{O^b})/2RT \quad (8)$$

In eqn. (8), $\mu_N^{O^m}$ and $\mu_N^{O^b}$ are the standard chemical potentials of cation N in the membrane phase and the external bulk solution, respectively, and $\mu_P^{O^m}$ and $\mu_P^{O^b}$ are the corresponding values of anion P. Using eqn. (4), the values of V_N and (X/K_N) can be determined from the ordinate intercept and initial slope of a plot for $1/t_-$ against $1/c_N^I$ at a given v .

Equation (4) indicates, that the intercept of a plot of $1/t_-$ against $1/c_N^I$ at fixed $v = 10$, allows the value of V_N to be determined. Plots of $1/t_-$ against $1/c_N^I$ for various 1:1 electrolytes are shown in Fig. 4 for both Nickel and cobalt Phosphate membranes. For the evaluation of (X/K_N) , the slope of eqn. (4), which is given by the following, is first determined

$$(V_N - l)((v - l)/v \ln v)(X/K_N)$$

The graphical value of the slope determined from Fig. 4 is equated with the above expression and then by substituting V_N , the value of (X/K_N) is determined.

The value of g_N is calculated from eqn. (9) at different concentrations (equation 39 of Toyoshima et al. (32) and)

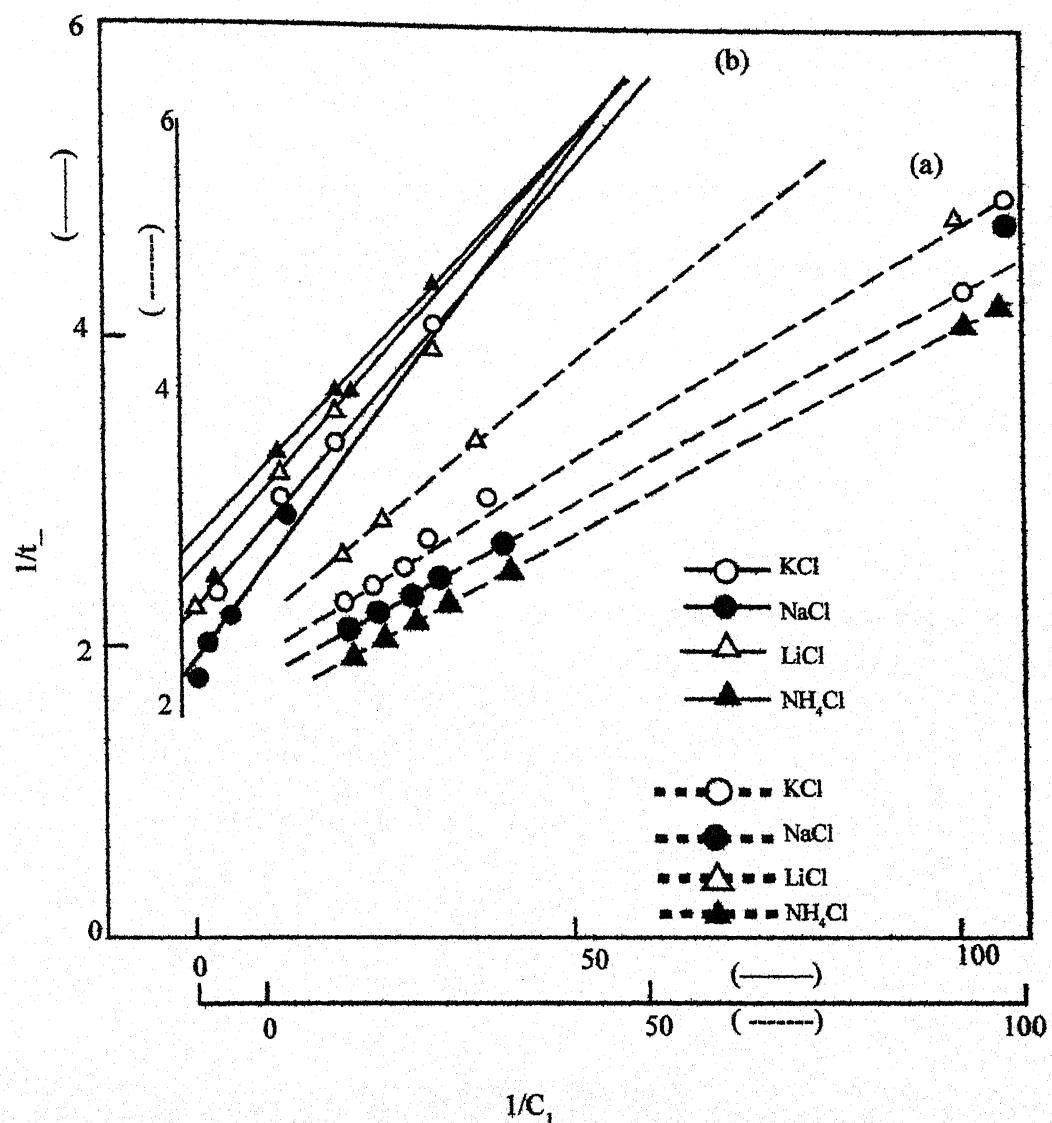


Fig. 4. Plots of $1/t_$ vs. $1/c_$ for (a) cobalt phosphate and (b) nickel phosphate membranes with various 1:1 electrolyte.

$$g_N = 1 + \{1 + (2 K_N c/X)^2\}^{1/2} \quad (9)$$

By substituting the values of V_N and g_N in eqn. (10) J , the reduced flux, is evaluated.

$$(2J+1) \ln(g_A + 2J/g_B + 2J) - \ln(JV_A + 1/JV_B + 1) - \ln(g_A/g_B) = 0 \quad (10)$$

With the help of these parameters namely V_N , (X/K_N) , g_N and J the theoretical BIP is calculated from the (Toyoshima et al. eqn. -38)

Which is shown here as eqn (11)

$$\Delta\phi = [2 \ln K_A / K_B + \ln(JV_A + 1)](F / RT) \quad (11)$$

These theoretical values of BIP thus obtained are plotted against $\log c$ and are shown by broken lines in Figs. 5 and 6. For comparison the observed values of BIP are also plotted and are shown by solid lines in the same graph. It is quite evident from the Figures that the agreement between the observed and theoretical values is quite fair.

Further, an equation for BIP was also developed by wilson (45) and Ilani (46), in which they used the effective charge density value (X) for the evaluation of theoretical bi-ionic potential (BIP) values. The bi-ionic potential ($\Delta\phi$) of the cell of the type shown in the experimental part of this paper has been related with the effective fixed charge concentration (X) is represented by the equation.

$$\Delta\phi = \frac{RT}{E} \ln \frac{\sqrt{1 + \left(\frac{X_{M_A}}{2a}\right)^2} - \left(\frac{X_{M_A}}{2a}\right)}{\sqrt{1 + \left(\frac{X_{M_B}}{2a}\right)^2} - \left(\frac{X_{M_B}}{2a}\right)} \quad (12)$$

where X_{M_A} and X_{M_B} are the concentrations of the fixed ions on the

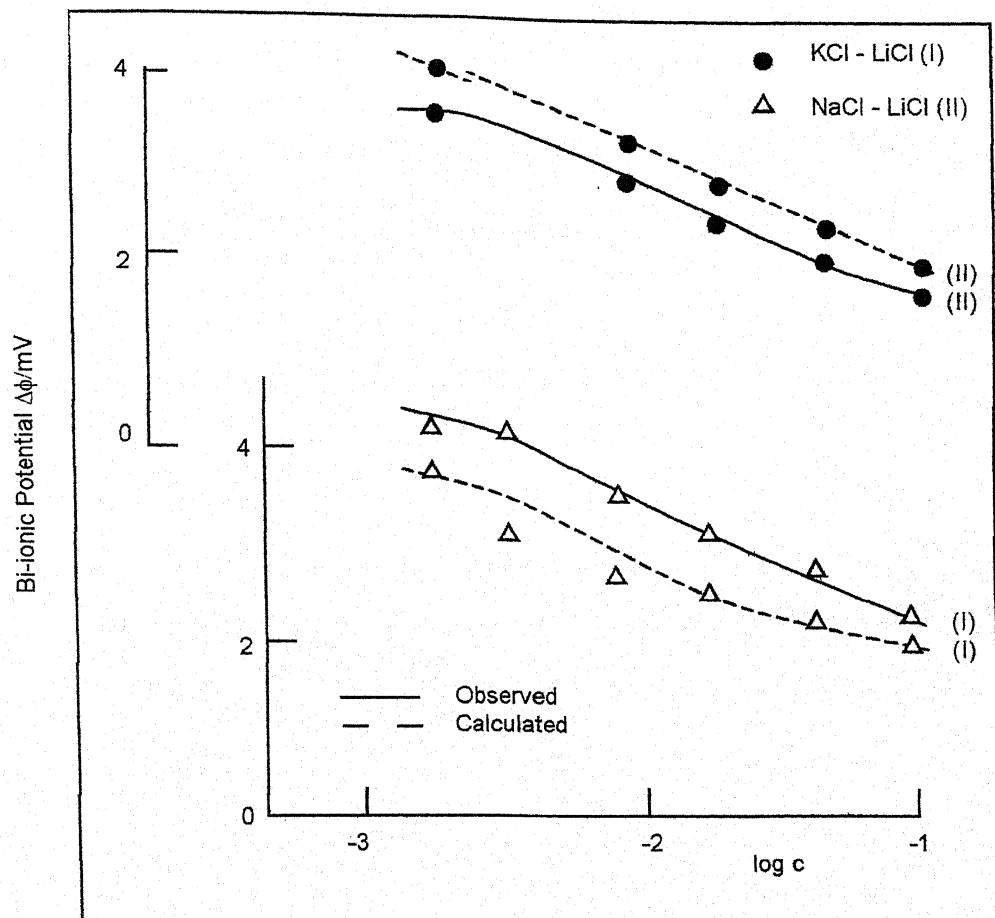


Fig. 5- Plots of observed (—) and calculated (---) bi-ionic potentials $\Delta\phi$ vs. $\log c$ for different pairs of electrolyte with cobalt phosphate membrane.

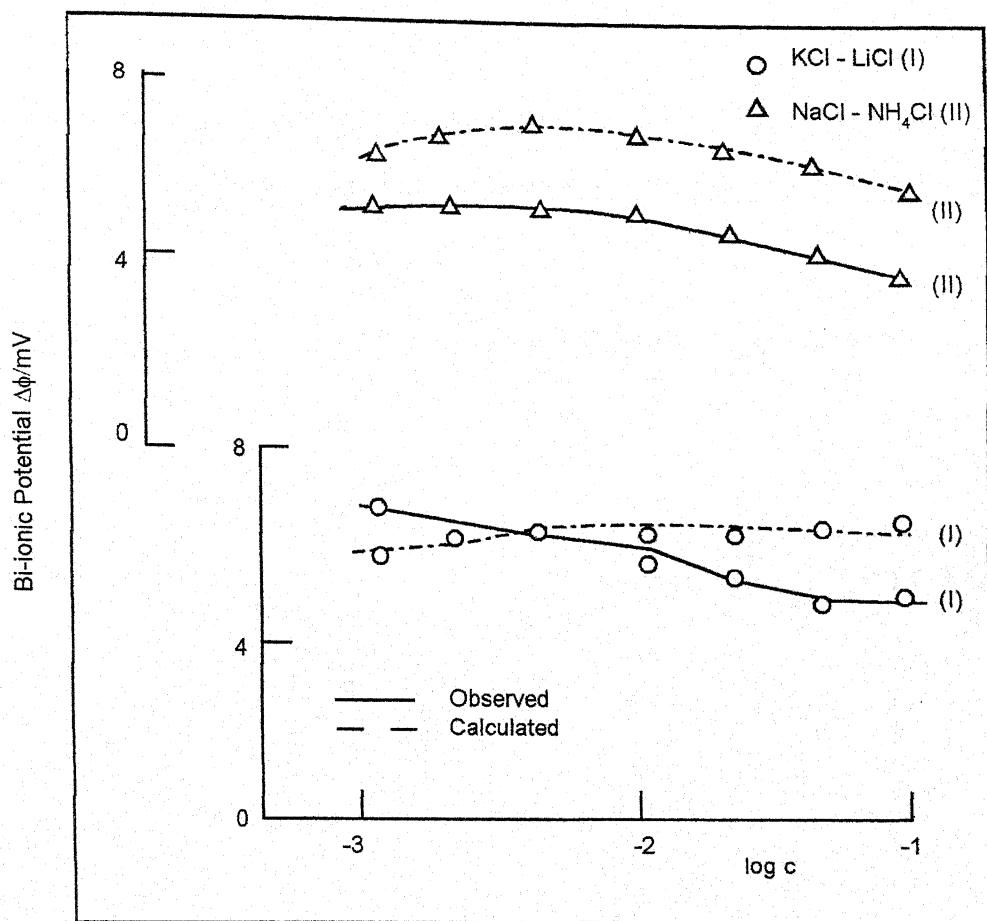


Fig. 6- Plots of observed (—) and calculated (---) bi-ionic potentials $\Delta\phi$ vs. $\log c$ for different pairs of electrolyte with nickel phosphate membrane.

membrane phase. Thus eqn. (12) can be used to calculated bi-ionic potentials across a membrane, provided effective fixed charge density of the membrane and the concentration of external electrolyte solutions are known. The values of bi-ionic potentials derived in this way from the predetermined values of X are given in table (5) and table (6). Thus, it may be concluded that the values of bi-ionic potential derived by the theory of Toyoshima and Nozaki (37) and with the use of predetermined value of effective fixed charge density (X) (Table -1) for both the membrane are similar to each other as well as comparable to the experimentally observed values of bi-ionic potentials for both inorganic precipitated nickel and cobalt phosphate separately.

Table 5

Bi-ionic Potentials, $\Delta\phi$ (mV) (Theoretical and Experimentally Observed) Across Nickel Phosphate Membrane

Bi-ionic Potential Electrolyte pairs	Experimental			Theoretical eqn (11)			Theoretical eqn (12)		
	KCl-NaCl	KCl-LiCl	NaCl-NaCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration									
0.1	3.0	3.0	2.9	3.1	3.1	2.8	3.0	3.0	2.5
0.05	3.5	3.3	3.2	3.2	3.1	3.0	3.4	3.0	3.3
0.01	4.1	4.0	3.5	4.3	4.1	3.2	4.0	4.3	3.8
0.005	4.5	4.1	3.9	4.1	4.2	3.6	4.6	4.4	3.5
0.001	4.7	4.3	4.2	4.2	4.0	4.3	4.3	4.5	4.0

Table 6

Bi-ionic Potentials, $\Delta\phi(mV)$ (Theoretical and Experimentally Observed) Across Cobalt Phosphate Membrane

Bi-ionic Potential Electrolyte pairs	Experimental				Theoretical eqn (11)				Theoretical eqn (12)	
	KCl-NaCl	KCl-LiCl	NaCl-NaCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl	
Concentration										
0.1	6.9	5.7	4.7	6.4	5.2	4.2	6.5	5.4	4.4	
0.05	7.1	6.2	5.1	7.3	6.0	5.0	7.0	5.9	4.9	
0.01	7.5	6.9	5.5	7.2	6.3	5.1	7.4	6.5	5.3	
0.005	7.8	7.1	5.8	7.4	6.9	5.2	7.5	7.0	5.4	
0.001	8.2	7.5	6.1	8.0	7.1	6.0	7.9	7.3	5.9	

REFERENCES

1. F. Helfferich, *Ion Exchange*, Mc Graw Hill, New York. (1962).
2. G. Schatchard, *Discuss. Faraday SOC*, 21, 30 (1956).
3. F.A. Siddiqi, M.N. Beg, S.P. Singh and A. Haque, *Electrochim. Acta*, 22, 631 (1977).
4. M.N. Beg, F.A. Siddiqui and R.S. Kushwaha *Can. J. Chem.* 55, 1680 (1977).
5. M.N. Beg, F. A. Siddiqi, R.S. Kushwaha and M. Arshad, *J. Membrane. Sci.*, 2, 365 (1977).
6. M.N. Beg, F.A. Siddiqi, R.S. Kushwaha and I. Altaf, *j. electroanal. Chem.*, 89, 141, (1978).
7. F.A. Siddiqi, M.N. Beg, and P. Prakash, *Ind. j. chem.*, 16A, 7, (1978).
8. F.A. Siddiqi, M.N. Beg, P. Prakash and S.P. Singh, *Indian J. Chem.*, 16A, 7 (1978).
9. F.A. Siddiqi, M.N. Beg, M.I.R. Khan, A. Haq, S.K. Saxena and B. Islam, *Can. J. Chem.*, 56, 2205 (1978).
10. R.S. Kushwaha, M.A. Ansari, N. Akhtar and P. Singh, *Ind. J. Chem.*, Vol. 31 A, 439 (1992).
11. M.A. Ansari, R.S. Kushwaha, A.K. Verma, and C.M. Gupta, *U. Scientist, Phyl. Sciences*, vol. 8, 1, 19, (1996).
12. F.A. Siddiqi, N. Lakshminarayanaiah and M.N. Beg, *J. Polymer Scl.*, 9, 2853, (1971) .

13. R.S. Kushwaha, H.P.S. Sengar, A. Gupta, R.Tiwari, and M.A. Ansari, Flora and Fauna, 4,2,93, (1998).
14. M.N. Beg, F.A. Siddiqi and R.S. Kushwaha , Can. J. Chem., 55, 1680 (1977)
15. R.S. Kushwaha, M.A. Ansari, A. Bhartiya, Chem. Environ. Res, 12, (384) 26, (2003)
16. R.S. Kushwaha, S. Agrawal and M.A. Ansari, J. Ind. council of chemist, Vol. 21, 2, 10, (2004).
17. N. Lakshminarayanaiah and F.A. Siddiqi, J. Polymer Sci, 8 (1970) 2949; Biophys. J., 11, 603 (1971), 12, 150 (1972) Z. Phys. Chern. (Frankfurt), 78, 150 (1972) in M. Bier (Ed.), Membrane Process in Industry and Biomedicine, Plenum Press, New York, P. 301, 1971,
18. A.M. Liquori and C. Botre, Ric. Sci, 34, 6 (1964), J. Phys. Chem., 71 3765 (1967).
19. T. Teorell, Proc. Soc. Exptl. Biol. Med., 33, 282 (1935); Proc. Natl. Acad. Sci (U.S.), 21, 152 (1935) Z. Elektrochem., 55, 460 (1951) Progr. Biophys. Chem., 3, 305 (1953) Discuss. Faraday Soc., 21, 9 (1956).
20. K.H. Meyer and J.F. Sievers, Helv. Chim. Acta, 19, 649, 665, 987, (1936) .
21. G. Schmid, Z. Elektrochem., 54, 424 (1950), 55, 229 (1951) 56, 35 (1952) G. Schmid and H. Schwartz, Z. Elektrochem., 55,295 (1951), 56, 35 (1952).

22. K. Sollner, J. Phys. Chem., 49, 47,171 (1945), J. Electrochem. Soc., 97 (1950) 139; Ann. N.Y. Acad. Sci., 57, 177 (1953); J. Macromol. Sci, A3, 1 (1969).
23. H.P. Gregor, J. Amer. Chern. Soc., 70, 1293 (1948); 73, 642 (1950).
24. G. Eisenman in A. Kleinzelrs and A. Kotyk (Eds.), Membrane Transport and Metabolism, Academic Press, New York, 1961, p. 163; Biophys. J., 2, 259 (1962).
25. H. Sherry in J.A. Marinsky (Ed.), Ion Exchange, Vol. 2, Marcel Dekker, New York, 1968.
26. O. Kedem and A. Katchalsky, Trans. Faraday Soc., 59, 1918, 1931, 1941 (1963).
27. K.S. Spiegler, Trans. Faraday Soc., 54, 1408 (1958).
28. G. Scatchard, J. Amer. Chern. Soc., 21, 30 (1956); Discuss. Faraday Soc., 21, 30 (1956).
29. F. Helfferich, Ion Exchange, McGraw Hill, New York, 1962.
30. R. Schlogl, Stoff transport durch Membrane, Dr. Dietrich Steinkopff Verlag, Darmstadt, 1964.
31. Kobatake, T. Noriaki, Y. Toyoshirna and H. Fujita, J. Phys. Chem., 60, 3981 (1965).
32. Toyoshima, M. Yuassa, Y. Kobatake and H. Fujita, Trans. Faraday Soc., 63, 2803, 2814 (1967); J. J. Phys. Chem., 72, 2871 (1968).
33. N. Kamo, Y. Toyoshima, H. Nozaki and Y. Kobatake, Kolloid-Z.Z.Polym., 249, 1061 (1971); 248, 914 (1971).

34. N. Kamo, M. Ockawa and Y. Kobatake, *J. Phys. Chem.*, 77, 92, 2995 (1973).
35. M. Nagasawa and I. Kagawa, *Discuss. Faraday Soc.*, 21, 52 (1956).
36. M. Tasaka, N. Aoki, Y. Konda and M. Nagasawa, *J. Phys. Chem.*, 79, 1307 (1975).
37. Toyoshima and H. Nozaki, *J. Phys. Chem.*, 74, 2704 (1970).
38. L.S. Hersh, *J. Phys. Chem.*, 72, 2195.419 (1968) L. Michaelis, *Kolloid-Z.*, 62, 2 (1933).
39. L. Michaelis, *Kolloid-Z.*, 62, 2 (1933)
40. C.E. Marshall and C.A. Krinbill, *J. Amer. Chern. Soc.*, 64, 1814 (1942).
41. K.H. Meyer and P. Bernfeld, *Helv. Chem. Acta*, 28, 962 (1945).
42. K. Sollner, S. Dray, E. Grim and R. Neihof, *Ion Transport Across Membranes*, Academic Press, New York, p. 144, (1954),.
43. G. Manecke, *Z. Electrochem.*, 55, 672 (1951).
44. M.R.J. Wyllie, *J. Phys. Chem.*, 58, 167 (1954).
45. J.R. Wilson, *Demineralization by Electrodialysis*, P. 84, Butterworths London & Washington D.C. (1960).
46. A. Ilani, *Biophys. Acta*, 94, 415 (1965).

Conclusion

CONCLUSION

The chapter "Charge Density of Membranes" is also a part of study of characterising the membranes. In this work, parchment supported membranes made of nickel phosphate and cobalt phosphates by the method of intraction used to observe membrane potential values (E_m) across both the membranes. When they are used to separate electrolyte solution of different concentrations, indicate the presence of charge on membrane matrix. The change of (E_m) values in reverse order of electrolyte concentrations suggests the reversal of membrane charge and selectivity of phosphate membranes which is not seen in our earlier findings. However, it is an interesting indication for both nickel and cobalt phosphate membranes that the membranes are cation selective when separating dilute solutions and anion selective while separating concentration solutions.

On the other, the transference number (t_-) of co-ions through the membranes increases from high to lower concentration of electrolytes indicates the preferential salt adsorption which is infact, the charge distribution on membrane sites in turn. Simultaneously, the apparent transference number (t_{app}) approximately similar to (t_-) for co-ions are seen important factors for the evaluation of effective fixed charge density (X) values the estimation of permselectivity P_s values with the support of t_- and t_{app} both, were seen very effective towards X determination. At the last, the thermodynamically fixed charge density (X) values of both the membrane system individually by using

different methods were found low, which indicated that both the membranes have stable fixed charge distribution in their phase.

Transport phenomena under the head of "Diffusion of electrolytes" were found very much challenging to recently burning problems. After the fabrication of the parchment supported inorganic precipitate membranes of nickel and cobalt phosphate separately, membrane potential and membrane resistance were observed experimentally at different temperatures after definite intervals of time in order to study of permeation of electrolytes as cations/anions across both the membranes with the help of recently developed theories. The membrane resistance R_m for both the membranes at any given time for metal ions and alkali earth metal ions in sequence as : $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ and $\text{Ba}^{++} > \text{Ca}^{++} > \text{Mg}^{2+}$ and also for aluminum ion refers that very few coions are in membrane phase. On the other hand, the effect of charge on cation is seen an important factor towards the mobility of cations across both the parchment supported membrane. Besides of the membrane potential, the sequence of monovalent cations i.e. $\text{Li}^+ > \text{Ka}^+ > \text{K}^+$ and di-valent/tri-valent cations i.e. $\text{Al}^{3+} > \text{Ba}^{++} > \text{Ca}^{2+} > \text{Mg}^{2+}$ also points towards the adsorption of these ions on membranes matrix. The slight changes of membrane potential (E_m) and membrane resistance (R_m) are considered due to the nature of ions and membrane effected during the adsorption.

The values of diffusion rate dQ/dt for various cations of both the membranes calculated from the values of membrane potential (E_m) and

membrane resistance (R_m) are found slower than in free solution which is the attribution of interaction of diffusing species with the fixed charge groups on the membrane matrix. The diffusion rate sequence of cations diffusing through both the membranes was $K^+ > Na^+ > Li^+$ and $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$, which on the basis of Eisenman Sherry model of membrane selectivity can be seen, because of weak field strength of charge groups attached to the membrane matrix. However, use of absolute reaction rate theory towards the evaluation of thermodynamic membrane parameters in which negative values of entropy change, ΔS° , indicate the mechanism of flow of coions /counter ions as interstitial permeation of the membrane (Minimum Chain loosening) with immobilization in the membrane (small zone of disorder). Here, both membranes show same behaviour towards the diffusion of different electrolytes. Hence, it is concluded that membrane solution interface is the rate limiting step for permeation.

The last one, that is, chapter IIIrd a "Bi-ionic Potential Studies" also adds some facts regarding the characterization of both the parchment supported nickel and cobalt phosphate membranes in the light of bi-ionic potential (BIP) theories. Since bi-ionic potential (BIP) is a measure of selectivity of a membrane for ions of the same sign. Upon the application of recently derived equation by Toyoshima and Nozaki for BIP and Membrane potential on the basis of non equilibrium thermodynamics, using appropriate assumptions for the mobilities and activity coefficients of small ions in membrane phase to our

system of parchment supported membranes, the theoretical values of BIP were evaluated with the help of thermodynamic parameters. However, the effective fixed charge density (X) values of the membranes obtained by various methods, on one side represent the membrane character while on other side contributes in the evaluation of theoretical values of BIP. The interesting result which is seen here is that, the experimentally observed values of BIP for both the membranes have good agreement with the theoretical values. As a result, both the parchment supported phosphate membranes turn to be effective for enrichment of desalination, separation processes etc. on the behalf of these findings.

Summary

SUMMARY

Transport phenomena occurring across parchment supported membranes have been thoroughly investigated by taking into account the following aspects, namely (i) ionic transport, (ii) membrane potential, (iii) electrical conductivity, (iv) ionic distribution equilibria and (v) spatial distribution of ions and the potential within the membrane.

The work described in the thesis has been divided into following three parts.

Part I deals with the characterization and evaluation of effective fixed charge density of parchment supported nickel and cobalt phosphate membranes from membrane potential measurements using various 1:1 electrolytes at different concentrations. The following methods : (i) Teorell-Meyer and Sievers method, (ii) the methods developed by Kobatake and co-workers and (iii) the most recently developed method of Tasaka et al. based on the principles of irreversible thermodynamics for the evaluation of charge density values were utilized.

The value of membrane potential measured across cobalt and nickel phosphate membrane with the use of the chlorides of K^+ , Na^+ and Li^+ were all positive when the membrane was used to separate dilute solutions of the electrolytes (dilute solution side taken as positive). This means that the membranes were cation selective, and when the membrane was used to separate concentrated solutions the values of E_m were negative, that is the membrane became anion selective. This type of reversal in selectivity character is not peculiar to these systems. In the case of cobalt and nickel phosphate membranes the membrane potential values were positive at all the

electrolyte concentrations showing thereby, that the membranes are cation selective.

For the evaluation of effective fixed charge density Teorell-Meyer and Sievers (TMS) derived a theoretical equation for membrane potential when a charged membrane separates different concentrations of an electrolyte by considering a diffusion potential within the membrane and two interfacial potentials at the membrane solution interfaces. The membrane potential equation thus derived has been generally accepted and widely used for the evaluation of effective fixed charge density and mobility ratio of the ions within the membrane by the plotting method. The method gave quite satisfactory results.

Kobatake, Nozaki and others derived the equation for membrane potential on the fixed charge concept by utilizing a number of basic assumptions. The two limiting forms of the equation were derived and used for the evaluation of fixed charge density of the membranes. It was interesting to note that the theoretical predictions were borne out quite satisfactorily by our experimental results with both the membranes used for the investigations.

Another equation for membrane potential derived by Kobatake and Kamo, similar to the TMS equation was used for the evaluation of thermodynamically effective fixed charge density of the membranes. This method involves the use of apparent transference number of coions and permselectivity P_s of the membranes. In this method, permselectivity calculated from apparent transference number was plotted against $\log (C_1 + C_2)/2$, the concentration at which P_s becomes $1/\sqrt{5}$ gave the value of the thermodynamically effective fixed charge density of the membrane.

Most recently Taksaka, Nagaswa and Co-workers derived another equation for membrane potential when a charged membrane separates two solutions of an electrolyte based on the principles of the irreversible thermodynamics. At sufficiently high electrolyte concentrations the equation reduces to a suitable form which is used for the evaluation of effective fixed charge density of the membrane by the plotting method. Thus the values of effective fixed charge densities evaluated from different methods were identical which not only confirm the stability of the membranes but also recognize the recently developed membrane theories.

Part II deals with the preparation of new system of parchment supported cobalt and nickel phosphate membranes and the studies of diffusion of a number of 1:1, 2:1 and 3:1 type of electrolytes through them. Various membrane parameters, namely, membrane potential E_m , cationic potential E^+_c and membrane resistance R_m etc. have been determined with the electrolytes at different concentrations by electrometric method. The diffusion rates were computed using the recently developed equation by Kittleberger based on the simple laws of electrolysis and utilizing the derived membrane parameters, the diffusion rate sequence derived at $25 \pm 0.1^\circ\text{C}$ was as follows: $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ and $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{Al}^{3+}$. The diffusion rate sequence of the membrane for various uni, bi and trivalent cations were found to be primarily dependent on the differences in the hydration energies of Counterions in the external solution. On the basis of Eisenman-Sherry theory of membrane selectivity, this diffusion rate sequence of alkali metal cations point towards the weak field strength of the fixed charge groups on the membrane matrix.

Various membrane transport parameters at different temperatures were also evaluated and the energy of activation E_a for the diffusion of electrolytes were calculated. It was found that the values of E_a for diffusion through the membranes were higher than those found for diffusion in free solution.

The theory of absolute reaction rates was applied for the diffusion process and the various activation parameters namely, enthalpy of activation ΔH^* , free energy of activation ΔF^* , and entropy of activation ΔS^* were evaluated. The values of ΔS^* were found to be negative indicating thereby that the diffusion takes place with partial immobilization in the membrane phase. The relative partial immobility was found to increase with increase in the valance of the ion constituting the electrolyte. A formal relationship between ΔH hydration, ΔF hydration and ΔS hydration of cations with the corresponding values of ΔH^* , ΔF^* and ΔS^* for diffusion was also found to exist for these membranes.

The Part III of the thesis contains the studies of the selectivity of the membranes for the cations due to the presence of specific charge in the membrane matrix with the help of experimentally observed values of Bi-ionic or Multi ionic membrane potentials using the membrane potential, Bi-ionic potential or Multi ionic potential theories. In the charged membranes, the co-ions are excluded from the membrane phase and only the counterions diffuse through the membrane, when it is interposed between two different electrolyte solutions of same concentrations. A quantitative description of the phenomena arising across an ion exchange membrane when two different

counterions (bi-ionic) or more (multi-ionic) diffuse through the membrane was given by Helferich. Mathematically, regorous equation were derived on the basis of the thermodynamics of irreversible processes by Helferich and scatchard and used them preferably only for cation selective (anion selective) membranes separating mixtures of uni-univalent electrolytes with a common anion or cation. However, author would like to say that the chapter mainly deals with the application and test of the most suitable theories of membrane potential developed by Nagasawa et al. based on the principles of irreversible thermodynamics as well as those of Toyoshima and Nozaki on bi-ionic potential.

After having prepared the parchment supported membranes of nickel and cobalt phosphate, the values of membrane potential and bi-ionic potential were observed experimentally using 1:1 electrolytes solutions. For membrane potential measurement the concentration difference of same electrolyte solutions towards opposite sides of the membrane was kept by 10 i.e. ($C_2/C_1 = 10$) while in bi-ionic potential measurements concentration was kept same but the electrolyte solution were taken different.

Initially effective charge density values of both the membranes were evaluated using the membrane equations derived by Tasaka et al. for negatively charged membranes. The equation for membrane potential ($\Delta\phi_m$)

$$-\Delta\phi_m = (RT/F) \left[\frac{v}{v-1} \right] (x/2) \frac{1}{c_1} + \dots$$

was used in the limit of high electrolyte concentration. The values of fixed charge on membranes were evaluated by graphical method. The

transport number of cations or anions across the membranes were also obtained using the Harsh's equation by substituting the values of charge density X and mobility ratio \bar{u}/\bar{v} which have already been evaluated. In fact bi-ionic potential is the measure of selectivity of a membrane for ions of the same sign. Therefore, recently derived equation by Toyoshima and Nozaki for BIP and membrane potential based on the principles of non-equilibrium thermodynamics, using appropriate assumptions for the mobilities and activity coefficients of small ions in the membrane phase applied here to our system of parchment supported membranes.

The theoretical parameters namely V_N , (X/K_N) , g_n and J were calculated using the various equations derived by Toyoshima and Nozaki as are given in contex. Using these values of the parameter in the given BIP equation, the theoretical BIP values were calculated. These theoretical values of BIP thus obtained were plotted against the concentration of electrolytes for the comparison with the observed values of BIP in the same graph. It is quite evident from the figures that the agreement between the observed and theoretical values is quite fair and it may be concluded that the theory of BIP developed by Toyoshima and Nozaki is applicable to our system of parchment supported nickel and cobalt phosphate membrane. These results are not only the test of recently developed membrane theories but also one of the way of characterization of these newly prepared membrane.

Publication

LIST OF PUBLICATION

- 1- Transport of Studies of Metal Ions Through Model Membranes with the application of absolute reaction rate theory, Proc. Natl. Semi., BRAMUW, p. 75 (2005) India.
- 2- Studies with Parchment Supported Membranes : Test of Membrane potential theories and the Evaluation of Membrane Selectivity of Metal Ions, J. Ind.Council of Chemist, (2006) (In press.)